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introduction to

AN INTRODUCTION TO METALLIC CORROSION

BY

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PREFACE

For about fifteen years, there has been no scientific book on the rrosion of Metals of a length suitable for continuous reading. Certainly ere have appeared, on each side of the Atlantic, several new works, cluding my own “ Metallic Corrosion, Passivity and Protection ” (1937, 38, 1946) ; but either these have been long books, intended for reference rposes, or they have covered only part of the subject.

The absence of a short book has made teaching difficult, and in more an one University efforts have been made in recent years to obtain cond-hand copies of my first small book on “ The Corrosion of Metals ” 924, 1926). But surely it is wrong, in a subject which is advancing so pidly as metallic corrosion, to ask students to read a book twenty ars old. Consequently, after finishing the new edition of the larger rk, I gave serious consideration to the possibility of producing a smaller e. Although extremely anxious to return to some promising experi- ental research which had long been held up, I decided to make an fort to provide an account of Corrosion short enough to be read from art to finish within a reasonable time.

The present volume is the result of this effort. It is an entirely new ok, having nothing in common with the former small “ Corrosion of etals ”, although a few passages have been copied from the large Metallic Corrosion, Passivity and Protection ”, since I did not feel able improve on the wording. Most of the diagrams have appeared either “ Metallic Corrosion, Passivity and Protection ” or in my four-volume ok “ Metals and Metallic Compounds ”. The arrangement differs con- lerably from that of my earlier books, and has been chosen to aid nderstanding even at the expense of strict consistency ; matter which, om a study of the Table of Contents, might seem appropriate to one apter, has sometimes been placed in another because it will be better nderstood in the position allotted to it.

I am hopeful that the book will be read, not merely by students, but experienced scientists who have hitherto taken no interest in the sub- ct of corrosion. It is my belief that to-day, although the understanding corrosion processes possessed by those investigating the subject is far ider than was the case in 1926 and the measure of agreement is highly tisfactory, the knowledge of the subject possessed by the general body of ientists is actually more limited than twenty years ago. Even some ho are closely concerned with corrosion problems in engineering and dustrial practice know very little of the scientific causes of corrosion actions. Among pure scientists, many think that the subject possesses scientific interest, whilst some seem to believe that corrosion reactions ey no well-defined laws ; actually laws exist, many of them simple d capable of ready interpretation ; they certainly present apparent differences from the laws which govern the more fashionable parts of chemistry, but that should surely add to their interest. It may be that the present neglect of chemical reactions involving both metals and non-metals (which, for lack of a better name, have come to be known as "corrosion reactions") is largely due to the non-existence of a book suitable for continuous reading. I shall be disappointed if the present volume does not do something at least to rectify the situation, and awaken interest in this *terra incognita* among those engaged in other branches of science.

I have opened with a historical note, since the subject is not afterwards treated chronologically; readers previously unacquainted with Corrosion may prefer to read this note *after* the rest of the book. It is followed by an introduction on electrochemistry—a knowledge of which science is absolutely necessary for the understanding of corrosion processes. The body of the book is divided into eight chapters. Each of these could probably be finished by a determined reader in a single evening, so that the book as a whole should be capable of being absorbed in a few weeks.

Whilst this is essentially a scientific book, I have illustrated basic principles by examples taken from engineering or industrial practice, which may serve to increase the interest of the subject to engineers or industrial chemists. It would be dangerous, however, to regard so short a book as a guide to practical preventative measures, since, for reasons explained in it, protective processes, unless correctly adjusted, may often make matters worse. Those faced with such problems should consult my larger book—or, better still, the original papers quoted in it.

In order to make the book more suitable for continuous reading, and to throw open the subject to those without serious mathematical training, I have, in the first seven chapters, introduced only a few simple equations. Practically the whole of the statistical and mathematical treatment has been segregated in the last chapter. Doubtless a few readers may elect to close the volume at the end of Chapter VII. On the other hand, it is not impossible that the discussion of elementary statistics in Chapter VIII may be found useful by persons unconcerned with the main subject of this book, since my other statistical writings have received a kind welcome from persons interested in several branches of science. This chapter contains some possibly novel features, such as the method of obtaining a distribution curve from data too limited for the clumsy and wasteful histogram procedure, the argument leading up to the probability integral in the *t*-test and much of the theoretical treatment of film-thickening and lateral spread; some of this has appeared in my recent papers but not in any book.

Instead of putting the references to the literature in footnotes, I have placed at the end of the volume a bibliography containing 168 numbered items; index figures inserted in the text show the number of the item to be looked up by those seeking fuller information on any subject. The papers and books cited represent neither the earliest nor latest writings on the subject, but merely statements which serve to amplify the matter under discussion. In case the reader has not easy access to a suitable library, he can usually obtain fuller information by looking up the subject in the index of the 1946 edition of my larger book (" Corrosion, Passivity and Protection "); but it should be recollected that the final proofs of that book were sent to the Printers some considerable time before the present small book was written, and that views on certain matters had developed during the intervening period.

My efforts to keep the book short have made necessary the omission of much which I would have liked to include. The valuable results of the tests organised by the Iron and Steel Institute Corrosion Committee have received less space than their intrinsic merits would seem to justify, but this work has already been admirably described by the Committee's Official Investigator, Dr. J. C. Hudson, in his book " The Corrosion of Iron and Steel ".

Clearly a book designed to meet the needs of several classes of readers must present some features unwelcome, and perhaps irritating, to each class. I must ask tolerance from those who are inclined to criticize the treatment either as childishly elementary or needlessly difficult.

Many chapters have been read at the typescript stage by a number of investigators now engaged in corrosion research at Cambridge; they include Dr. A. J. Gould, Dr. T. P. Hoar, Dr. J. E. O. Mayne, Dr. J. N. Agar, Dr. M. T. Simnad, Mr. A. U. Huddle, Mr. G. H. Noordhof, Mr. G. C. Smith, Mr. A. J. P. Tucker, Mr. D. Whitwham and Mr. M. J. Pryor; some of them have kindly looked through every chapter, and their suggestions have been most valuable. In addition, my friends Dr. W. H. J. Vernon and Dr. F. Wormwell, of the Chemical Research Laboratory, Teddington, have very kindly read the whole of the proofs at two different stages; I would express particular thanks for this assistance, given at a time when they were themselves most busy with important work.

Finally, I should like to express my thanks to Miss I. M. E. Cave for help in connection with the index.

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March 14, 1947.

HISTORICAL NOTE

The chronological sequence of scientific discovery is rarely the logical one. To arrange the facts of metallic corrosion historically would conceal the true interconnection existing between them, and thus deprive them of significance. Nevertheless, in view of the prevailing interest in the History of Science, many readers may welcome a short narrative showing how knowledge of the subject discussed in this book has grown. The note which follows should serve to indicate some names and dates associated with the advance of understanding, but it must be remembered that the credit for any particular discovery cannot be assigned to a single year or to a particular person. If a recent investigator is cited as the discoverer, objection may fairly be raised by the quotation from older papers of passages which seem to contain the germ of the idea; yet to allot the entire credit to early investigators may be unjust to later ones, who have established as facts what had previously been mere suggestions.

At the Dawn of History, the first metals to be used were those which were either found native, or could easily be reduced to the elementary state; such metals do not readily pass into the combined state, and their corrosion can have raised no serious problems. But with the introduction of iron, the problem of its corrosion must have presented itself, although it is an undoubted fact that some of the iron produced in Antiquity is to-day more free from corrosion than much of that manufactured in later years. This may have been due partly to the fact that iron reduced with charcoal contained less sulphur than modern steel, but it may also be connected with the absence of sulphur compounds from the air in the days before coal was adopted as a fuel; for it is often the conditions of early exposure which determine the life of metal-work. Whatever the cause, ancient iron has in some cases remained in surprisingly good condition for many centuries; the Delhi Pillar is the example which has excited most interest, but others could be quoted.

For many centuries there seems to have been little curiosity regarding the causes of corrosion, although a few significant observations were made. As early as 1788, Austin noticed that water, originally neutral, tends to become alkaline when it acts on iron. He attributed the alkalinity to the compound now called ammonia; this was probably an error, since the alkaline reaction produced by most saline waters is due to sodium hydroxide, the cathodic product of the electrochemical corrosion process.

The belief that corrosion is an electrochemical phenomenon was expressed in a paper published in 1819 by an anonymous French writer, thought to be Thénard, and in 1830 his compatriot, de la Rive, attributed the fact that acid attacks impure zinc more rapidly than the relatively pure varieties to an electric effect set up between zinc and the impurities present. Faraday's researches, especially those conducted between 1834 and 1840, afforded evidence of the essential connection between chemica action and the generation of electric currents; indeed (since his Laws o Electrochemical Action apply as much to anodic as to cathodic processes) he provided a quantitative basis for the observations of later investigators. One of the most interesting chapters of Faraday's work was concerned with the study of passivity—the subject of a famous correspondence in 1836 with Schönbein, then Professor of Chemistry at the Swiss University of Bâle (Basle). The experiments described suggested that the strange inactive condition which Schönbein had observed on iron was favoured by anodic action, but was often dispelled by cathodic treatment; this was all the more remarkable in that normally anodic action favours corrosion whilst cathodic action tends to prevent it.

After Faraday's time, interest in the electrical mechanism of corrosion processes seems to have waned. This may have been due to the fact that electrochemistry was hardly ready to be applied to the detailed elucidation of Corrosion, until the conception of Single Electrode Potentials had been made familiar by publications emerging from the schools of Ostwald and Nernst and culminating in an important paper by Wilsmore (1900). But in Great Britain, at least, attention may have been diverted by alternative suggestions ascribing corrosion to the presence or formation of certain substances. Some of these suggestions are now seen to possess a modicum of truth, but the underlying ideas are themselves consistent with an electrochemical mechanism.

Between 1888 and 1908 the view was frequently advanced that acids were the agents mainly responsible for corrosion; particularly it was held that the rusting of iron would only take place if carbonic acid was present. It was shown, however, by Dunstan, Jowett and Goulding in 1905, by Tilden in 1908, and by Heyn and Bauer in the same year, that iron exposed to water and oxygen, with exclusion of carbon dioxide, underwent rusting. Acid is not needed for the corrosion of iron, and indeed some of the most intense forms of attack take place in salt solutions which have been made definitely alkaline. There is, however, one important type of corrosion—that associated with the liberation of hydrogen—which occurs much more rapidly in acid than in neutral water; in atmospheric corrosion also, acid impurities in the air greatly stimulate attack upon iron, although they are not necessary for it. In such circumstances, therefore, the view that acid is an arch-promoter of corrosion may be held to be justified, but in atmospheric attack—as shown by Vernon—it is not carbonic but sulphurous acid which is mainly responsible; indeed Vernon (1935) demonstrated that under certain circumstances carbon dioxide can retard the attack upon iron.

Another theory of corrosion arose about 1900 as a result of the detection of hydrogen peroxide during the corrosion of many metals; this gave rise to the idea that it acted as intermediary in corrosion processes. It is now known that hydrogen peroxide may be formed in electrolytic cells where oxygen has access to the cathode. Consequently, if the electrochemical mechanism of corrosion is correct, the presence of traces of hydrogen peroxide among the corrosion products requires no further explanation.

Whilst British chemists were disputing the claims of carbonic acid and hydrogen peroxide to be regarded as the agents responsible for corrosion, the electrochemical standpoint was being developed in Sweden and elsewhere, especially in Arrhenius' laboratory by Ericson-Aurén and Palmaer, working separately and in collaboration from 1901 onwards. Their work dealt mainly with corrosion by those acids which act on metals eliminating hydrogen, and the results provided strong evidence that this attack was connected with the formation of microscopic cells, which they called " local elements ". Somewhat similar views were expressed by the American investigators Whitney (1903) and Cushman (1907) in their discussion of corrosion by neutral liquids.

The electrochemical views put forward by these writers overlooked, to some extent, the part played by oxygen, and broader theories of corrosion by neutral liquids, which recognized the function of oxygen as cathodic stimulator, were provided by the Americans Walker, Cederholm and Bent in 1907, and the Englishman Tilden in 1908. The most recent research, however, rather represents a return to earlier views, by indicating that oxygen is not absolutely necessary for the attack of water on iron. Experiments by the American investigators, Corey and Finnegan (1939) and de Kay Thompson (1940), suggest that iron is slowly attacked by oxygen-free water, with liberation of hydrogen, although in this case the final product is not yellow rust (ferric hydroxide) but black granular magnetite or sometimes ferrous hydroxide. The fact that at the boiling-point pure water, or even dilute alkali, could attack iron with liberation of hydrogen, was clearly demonstrated by the Germans, Thiel and Luckmann, in 1928, and was probably known at an earlier date.

Extensive researches into the facts of corrosion were carried out in Germany about 1908–10 by Heyn and Bauer, whose writings contain the germ of many ideas developed later. They were probably the first to carry out really comprehensive measurements of corrosion velocity in numerous liquids, embracing iron and steel in different conditions both alone and in contact with other metals. Amongst other things they quantitatively established the fact that attack upon iron was stimulated by contact with a nobler metal, whilst contact with a baser metal often conferred partial or complete protection (qualitatively this had long been believed to be the case, and indeed as early as 1824 Sir Humphrey Davy had proposed connection with iron or zinc as a means of protecting copper against sea-water). The behaviour of iron in contact with other metals was further studied at a later date. In 1924, Whitman and Russell demonstrated that when three-quarters of the surface of a steel specimen is coated with copper, the total corrosion by running water may remain the same as that of a similar specimen completely bare, but is now concentrated on the bare quarter. This experiment provided an illustration of the manner in which corrosion may be intensified when a small anode is connected to a large cathode, a matter also brought out by the author experiments in 1928, and by the extensive work of Akimow, with Clar and others, published in Russia about 1935.

Despite the importance of the so-called "galvanic currents" set u by dissimilar metals, the conception—prevalent up to about 1923—tha corrosion currents were generally due to dissimilar metals in contac e.g. the dominant metal and the impurities present in it, led to som erroneous conclusions. It spread the belief (definitely held by Palmaer that perfectly pure and uniform metal—if it could be obtained—woul be uncorrodible. Now in the hydrogen-evolution type of attack (whic Palmaer studied in his laboratory) impure metal really is attacked muc more quickly than the purer varieties, and the varying influence of differ ent impurities was afterwards brought out by the researches of the Czech Vondráček, and the Latvian, Straumanis. But this is not true of all type of attack; as pointed out in 1931 by the German scientist, Tammann impurities do not increase the rate of corrosion of zinc by a persulphat solution. Actually, electric currents can arise in other ways than by th contact of dissimilar metals; they can, for instance, be generated b differences in the liquid wetting different parts of a metallic surface notably by differences in the oxygen-content.

The fact that variations in oxygen concentration can set up electri currents should have been clear from the experiments of the Italian scientist, Marianini, performed as early as 1830, or from those of th German, Warburg (1889), and the Russian, Kistiakowsky (1908); bu the significance of these researches was largely overlooked. In 1916 however, the American, Aston, laid emphasis on the part played by loca differences in oxygen concentration in promoting the rusting of iron and in 1922 his fellow-countryman, McKay, showed that current could also be set up on a single metal by variations of metal ion concentration in the liquid.

Experiments carried out in the author's laboratory at Cambridge from 1923 onwards indicated that "differential aeration currents" (set up by differences in oxygen concentration) played an important part in the corrosion of many metals, although, as emphasized by Bengough, oxygen concentration is only one of many factors determining the potential existing at different points on a metallic surface. Considerable discussion as to the relative importance of different factors took place between the two groups of investigators associated with Bengough and the author respectively, and an agreed statement was published in 1938.

In the years 1931–9 the electric currents flowing over the surface of metal corroding in salt solutions were detected and measured by several of the author's collaborators at Cambridge, including Bannister, Hoar, Thornhill and Agar; also, after his return to America, by Mears, in collaboration with Brown. The currents were found to be strong enough to account for the whole of the corrosion actually measured, in the sense of Faraday's Law, and thus the electrochemical mechanism of corrosion by salt solutions may be said to rest upon a quantitative experimental basis.

Nevertheless, the increasing evidence for the electrochemical nature of corrosion by salts and acids led in some quarters to the exaggerated view that the mechanism of every corrosion process is necessarily electrochemical. No doubt any chemical change involves the displacement of electrons, but if we reserve the term "electrochemical corrosion" for those processes where current flows between anodic and cathodic areas situated at different parts of the metallic surface (with electrons flowing over paths long compared to the interatomic distance), then it is clear that many true corrosion processes are not electrochemical, since they occur in solutions where electrical conductivity is almost absent. The work at Cambridge has suggested that the reason why electrochemical action is so destructive is that it often leads to the formation of soluble compounds as the immediate corrosion products, whereas direct combination with oxygen often produces a sparingly soluble body in physical contact with the metal, thus stifling further attack. Frequently the electrochemical mechanism leads in the end to a sparingly soluble body, such as rust; but if this is formed as a secondary product through interaction between the anodic and cathodic products at a perceptible distance from the point of attack, there is no stifling and attack continues.

Actually in those cases where electrochemical action would produce a sparingly soluble body either at the cathode or at the anode, it stifles itself just like any other form of attack. Consequently it is possible to classify substances which stop corrosion by coating the anodic or cathodic parts with layers of sparingly soluble compounds as cathodic and anodic inhibitors. The Polish investigator, Chyżewski, working in the author's laboratory in 1938, made an experimental classification of inhibitors into these two groups. The anodic inhibitors are the most efficient, but are apt to be dangerous, since when added in insufficient amount they often reduce the area undergoing corrosion more rapidly than they diminish the total amount of corrosion, so that the intensity of the local attack is actually increased by the addition. It had been shown by the author in 1936 that this intensification was to be expected on theoretical grounds, and in recent years much work has been devoted at Cambridge to the search for an inhibitive system which will be both safe and efficient.

Many of the substances which form useful pigments in anti-corrosive paints probably act in rather the same way as the soluble inhibitors just discussed. This was indicated by the early work of Cushman and Gardner published in America about 1910. The distinction between inhibitive paints, which will prevent rusting even when the iron is left bare at a discontinuity in the coat, and the mechanically-excluding paints, which only give protection in so far as they prevent access of moisture to the metal, became increasingly clear in a series of field and laboratory tests, organized from Cambridge and carried out between 1930 and 1945, mainly by Britton, Lewis, Thornhill and Mayne. Another type of anti-corrosive paints which will give protection at gaps in the coats are those richly pigmented with zinc dust; here the exposed iron escapes attac largely because it is the cathode of the cell zinc/iron.

Although electrochemical corrosion will proceed where direct oxidatio would stifle itself, circumstances can arise in which this stifling does nc occur, and in such cases, corrosion need not take an electrochemica course. For instance, water containing oxygen may produce rusting if the conditions are such as to produce at the metallic surface the appreci ably soluble ferrous hydroxide, and to permit of its conversion to the les soluble ferric hydroxide (yellow rust) at a slight distance from the poin of attack, so that the rust is non-protective. Forrest, Roetheli and Brow (1930–1), in a series of instructive researches carried out at the Massa chusetts Institute of Technology, showed that rust coats varied in protec tive character according to the rate of supply of oxygen to the surface and the same principle was found to operate in statistical experiment with oxygen-nitrogen mixtures carried out by Mears (1935) during hi work in the author's laboratory. These indicated that oxygen can depres the probability of corrosion starting within a given area, although, wher once attack has set in, oxygen accelerates the corrosion rate; this distinction between corrosion velocity and corrosion probability has serve to clear up several of the apparent contradictions which puzzled earlie investigators.

The view has been advanced by several investigators that oxides of iron can in effect act as oxygen-carriers. In 1921 Friend, who had already carried out an extensive series of researches on the action of numerous salt solutions on iron, suggested that a colloidal solution of ferric hydroxide behaves as a carrier for oxygen, passing alternately between the ferrous and ferric conditions. Later (1936–8) Herzog attributed a rather similar rôle to "solid" rust, but combined this with an electrochemical mechanism. After long immersion in stagnant water, iron frequently becomes covered with an inner layer of magnetite, overlaid with an outer layer of ferric hydroxide. The magnetite is supposed to act as cathode towards the iron as anode, and the ferric hydroxide just above suffers cathodic reduction to hydrated magnetite. This may either lose water, reinforcing the magnetite, or may absorb oxygen from the air, returning to the state of ferric hydroxide. It seems very likely that under certain circumstances some such mechanism does operate. In any case, it is fairly certain that in the acid corrosion of iron, ferric salts can act as oxygen-carriers, being reduced to the ferrous state by the metallic iron, and then reoxidized by atmospheric oxygen, as indicated in the researches of Bryan (1934–5); cupric salts can perform a similar rôle in the attack of acids upon copper, as shown by Glauner in 1933.

The electrochemical study of passivity has been the subject of a long series of experiments started about 1927 in W. J. Müller's laboratory at Vienna, which has placed the mechanism of anodic passivation on a mathematical basis; he was aided by numerous collaborators, of whom Konopicky and Machu deserve special mention.

Most of the laboratory experiments mentioned above have been of hort duration, and have been concerned mainly with the opening stages of corrosion. In this respect, they were not entirely representative of natural corrosion processes, which continue for long periods. A feature of the extensive and very accurate work of Bengough, started about 1927, first in collaboration with Stuart, then with Lee and later with Wormwell, was the performance of experiments under strictly controlled conditions, extending over many years.

Whilst the mechanism of low-temperature corrosion was being investigated, high-temperature oxidation was also under study and here it was found possible to establish simple laws of growth. The scientific study of the oxidation process may be said to have begun with the classical work of Pilling and Bedworth published in 1923. The careful observations of Pfeil (1929–31), based on refined analytical work, showed that the growth of oxide consisted in the movement of metal outwards rather than the penetration of oxygen inwards through the scale. Further valuable information regarding the oxidation of iron and its alloys was obtained by the detailed metallurgical observations of the French investigators, Portevin, Prétet and Jolivet, published in 1934. About the same time, the German physical chemist, Wagner, was producing a number of papers, practical and theoretical, which showed that high-temperature oxidation is connected with the passage of cations and electrons outward through the growing scale ; low-temperature tarnishing, due to sulphur compounds in the air, follows a similar mechanism. A mathematical relationship was established between the oxidation rate and the electrical properties of the film substance ; this shows that good resistance to oxidation may generally be expected where the electrical resistance of the oxide formed is high. A new and instructive derivation of Wagner's equation was published by Hoar and Price in 1938, whilst in the same year Price and Thomas, working at Cambridge, applied these new theoretical ideas to the development of a process known as Selective Oxidation, which produces enhanced resistance of copper alloys to high-temperature oxidation, and similarly improves the behaviour of silver alloys towards low-temperature tarnishing. Shortly before this, Miley, also working in the author's laboratory, developed an electrometric method for measuring the thickness of oxide films, depending on the quantity of electricity needed for their reduction, and was thus able to obtain curves showing the early stages of the rapid growth of invisible films on iron and copper exposed to air at ordinary temperatures. A very complete study of the oxidation of zinc over a range of temperature by Vernon, Akeroyd and Stroud was published in 1939.

Our knowledge of oxidation has been aided by the examination of the oxide films. Here X-rays and, more particularly, electron diffraction methods, have been most helpful ; the work of Finch and Quarrell (1933–4) on electron diffraction methods deserves special mention. Less well known, but holding great promise, are the optical methods depending on the changes in the ellipticity of polarized light reflected at a metallic surface—changes which are themselves modified when a film is present on the metal. This method, which in suitable cases provides information both of the thickness and refractive index of the film, was first used to study oxide films in Freundlich's laboratory in Berlin (1927), was elaborated by the Norwegian physicist, Tronstad (1929–34), and has been further improved by Winterbottom; in a different form it was used by Leberknight and Lustman in Mehl's laboratory at Pittsburgh about 1939. Other optical methods for obtaining the thickness of films depend on interference. The simplest of these methods was used by Tammann in his classical studies of the laws of film-growth in the years 1920–6, whilst later a more accurate spectroscopic method was employed at Cambridge by Constable (1927–9).

Further information has been obtained by the author alone (1927), and with J. Stockdale (1929), by stripping the films from metal, or, as in his later process (1938), by their transfer to transparent plastic; films which produce interference tints on the metal usually display complementary colours after transfer. (The method of Stockdale and the author has recently been used by Phelps, Gulbransen and Hickman in their application of the electron microscope to the study of films stripped from several metals.) A form of film-stripping suitable for the chemical estimation of the constituents was developed by Vernon, Wormwell and Nurse in 1939, who established the fact that the polishing of the surface of stainless steel leads to an enrichment of chromium, the protective element, in the surface film; evidence of analogous cases of enrichment had been obtained in 1938 by the Polish investigator, Dobinski, using the electron diffraction method.

Another field of research which has been developed concurrently is that of atmospheric corrosion. Vernon's extensive and accurate studies of the behaviour of metals exposed to the atmosphere, published at intervals from 1923 onwards, established simple laws connecting corrosion and time. One of the important results attributable to Vernon, Hudson and Patterson was the Principle of Critical Humidity; it was found that frequently corrosion only became rapid in air when the humidity exceeded a certain value.

Very extensive atmospheric corrosion tests have been carried out for various Committees on both sides of the Atlantic. The American Society for Testing Materials were pioneers in this field, and have accumulated a quantity of valuable data. Particularly impressive are the results obtained by J. C. Hudson (1929–45), working first on non-ferrous metals for the British Non-Ferrous Metals Research Association, and then on ferrous metals for the (British) Iron and Steel Institute. Hudson's extensive researches have established the relative resistance of different materials in numerous different atmospheric conditions, and in the case of iron and steel have indicated how best protection can be achieved by coatings of paint or non-ferrous metal.

Up to about the time of the war of 1914–18, most of the experimental work on corrosion had been conducted by pure scientists. In later years, a serious increase in the frequency of breakdowns due to corrosion led to the inception of a number of technical researches on industrial problems. In Great Britain some were started by individual firms, but most by research organizations receiving support both from the Government and the interests concerned. A good example is the work on the corrosion of condenser tubes sponsored first by the Corrosion Committee of the Institute of Metals, whose first report appeared in 1911, and later by the British Non-Ferrous Metals Research Association. The experimental work was carried out in the early years by Bengough and several colleagues, one of whom, May, took over the leadership when Bengough passed on to other branches of corrosion research. Condenser trouble had been so serious in the war of 1914–18 that at one time it was causing the British Admiralty more anxiety than the enemy's fleet. Largely as a result of the work of Bengough, May, and their colleagues, along with the industrial development of new corrosion-resisting alloys, the position so much improved that in the war of 1939–45, condenser trouble, although not unknown, caused little anxiety.

Naturally researches dealing with any technical problem have tended to be carried out in countries where the problem in question has arisen. Thus marine corrosion has been extensively investigated in Great Britain, corrosion troubles in hydroelectric installations have received attention in Switzerland and Northern Italy, the bacterial attack upon pipes buried in clay soils was first studied in detail by the Dutch bacteriologist, von Wolzogen Kühr, whilst special methods of protecting long pipe-lines have been worked out in the United States.

Industrial necessity has led to the investigation of many points which the pure scientist would probably have overlooked. It is somewhat doubtful whether a programme of pure science research would have established the fact that chemical and mechanical stress operating together can cause more weakening than when they operate separately. The mechanical stresses may be internal or applied. An early example of corrosion favoured by internal stresses was the so-called season-cracking of cold-worked brass in an atmosphere containing ammonia. This received study in many countries, but the extensive work of Moore and Beckinsale in 1920–3 not only established the conditions favourable to intergranular cracking, but also indicated the means of avoiding the trouble. Types of intergranular cracking connected with stresses occur on steel exposed to hot alkaline water (as in some power boilers) or in hot nitrate solutions ; these have also received study in many countries—rather especially in the United States. Very important, in view of the development of aircraft, is the stress-corrosion cracking of certain aluminium alloys. The views held to-day owe much to the Russian investigator, Akimow, the American group associated with Dix, the British group led by Sutton, the Swiss metallurgists, von Zeerleder and Bosshard, and the German investigator, Bollenrath.

Especially dangerous is the combination of alternating stress and corrosion, producing the trouble known as corrosion-fatigue. This was observed during the war of 1914–18 on paravane towing ropes, and Haigh was the first to ascribe their rapid failure to conjoint chemical-mechanical action. About 1926 the American investigator, McAdam, commenced an extensive set of elaborate tests on corrosion-fatigue ; his earlier results were brought into a convenient compass by Gough in a lecture delivered in 1932. The scientific aspect of corrosion-fatigue has been under investigation for some years at Cambridge by Gould (1934–9), and later by Huddle and Tchorabdji Simnad.

Great importance attaches to the intergranular attack on austenitic stainless steel, met with most frequently in the neighbourhood of welds. Here an intergranular network deficient in chromium (and therefore anodic to the main part of the metal) appears to be the cause of the trouble ; evidence was supplied by the photomicrographic work of Bain, the electrical measurements of Mears, Fink and Brown, and the analytical observations of Schafmeister and of Sy.

The researches on corrosion undertaken for technical reasons have often advanced the scientific understanding of the mechanism, and indeed Committees which have sponsored the technical researches have also arranged generous support for work in universities and elsewhere devoted to the scientific causes of the phenomena. The activities of Hatfield, for instance, were equally fruitful in promoting investigations of immediate industrial value and in supporting researches of a more academic character. Nevertheless, the prominence given to the technical aspect of corrosion has tended in recent years to spread the idea that the subject is simply a commercial one, and, perhaps for that reason, interest in the mechanism of the reactions between metals and non-metals has considerably waned among pure scientists during the last thirty years. Thus, although the kinetics of such reactions are in many cases well established, and obey relatively simple laws for which a logical interpretation can usually be provided, it is a strange fact that to-day such laws receive no attention in most textbooks of chemical kinetics, and often remain unmentioned in lectures on physical chemistry given to students.

Possibly it is really the strangeness of corrosion reactions which causes the orthodox physical chemist to regard the whole subject with suspicion. The type of procedure which he has come to apply almost automatically to each new problem—the measurement of a temperature coefficient followed by the calculation of some energy of activation—is not of immediate service in a subject where Geometry, and not Energetics, controls the situation, and where the velocity of a reaction often diminishes as temperature rises. This does not mean, of course, that the principles which govern the rest of chemistry become invalid in corrosion, but there is clearly need for some hard thinking before their significance becomes apparent. Particularly those who regard Thermodynamics as the bedrock of science feel they are in the quicksands, since many corrosion reactions—thermodynamically possible—do not in practice occur because the corrosion product stifles them by isolating the reactants. Nevertheless, Thermodynamics, applied to corrosion by those who are masters in both fields, can yield most fruitful results, as shown by the work of Gatty and Spooner and of Warner, and recently by that of the Belgian, Pourbaix.*

The artificial exclusion of certain types of chemical reactions from the purview of the scientific chemist is not only discouraging to those working in the subject excluded, but is unfortunate for the science of chemistry, since it leads to a false picture of the whole situation. To some extent, however, this neglect may be due to the fact that the established facts of corrosion processes cannot readily be found collected in a book of convenient size. If this little volume should succeed in bringing the subject to the attention of chemists and physicists who have hitherto taken no interest in it, it will not have been written in vain.

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* Pourbaix's outstanding work is hardly known outside his own country. My colleague, Dr. J. N. Agar, is preparing an English translation of his book.

ELECTROCHEMICAL INTRODUCTION

General

Importance of Electrochemistry. So many corrosion processes are electrochemical phenomena that a knowledge of scientific electrochemistry is essential for the understanding of corrosion. This introduction may help readers whose knowledge of the subject needs refreshing, but all who can afford the time are strongly advised to study a standard electrochemical textbook.[65]

Faraday's Law. If an electric current of I amperes is made to pass through an electrolytic cell, consisting of two metal electrodes immersed in a solution of an electrolyte, then, in the absence of secondary effects, the velocity of the corrosion suffered by the anode will be I/F gram-equivalents per second, where F is Faraday's Number (96,487 coulombs per gram-equivalent). This means that 1 ampere hour will dissolve 1·04 grams of pure iron (as ferrous salt), 1·22 grams of zinc or 3·86 grams of lead.

Ohm's Law. If the effective E.M.F. driving the electrolytic cell is E volts, the current in amperes (I) will be E/R, where R is the resistance of the cell in ohms; the corrosion velocity will be E/RF. However, in most practical cases, the E.M.F. causing corrosion is not applied from an outside source, but is furnished by the metal itself; owing to " polarization " the value of E tends to diminish with the current density (current per unit area), and the state of affairs becomes complicated.

Generation of Electric Currents. It is known — largely from photo-electric research—that the energy needed to remove an electron from a metal varies greatly in different cases; in general, the removal requires more energy in the case of a noble than a base metal. If two metals, say copper and zinc, are placed in contact, the copper will (in absence of complicating factors) tend to absorb electrons from the zinc until the potential difference set up by the transfer is sufficient to oppose further passage of electrons across the interface. It is, of course, impossible to obtain a continuous electric current from a circuit consisting half of zinc and half of copper (Fig. 1(*a*)), since the potential difference (P.D.) set up at one contact (P_1) will exactly balance that set up at the other (P_2)—provided that the two contacts are kept at the same temperature. If, however, the zinc and copper are joined through a solution of, say, potassium chloride (Fig. 1(*b*)), a current can be generated, the energy being provided by chemical changes. The passage of electricity across the liquid will consist in the movement of *negatively* charged *anions* (each bearing an extra electron) towards the zinc, which is the *anode* of the cell (the pole towards which the anions move), and the movement of *positively* charged *cations* (atoms deficient of an electron) towards the copper, which

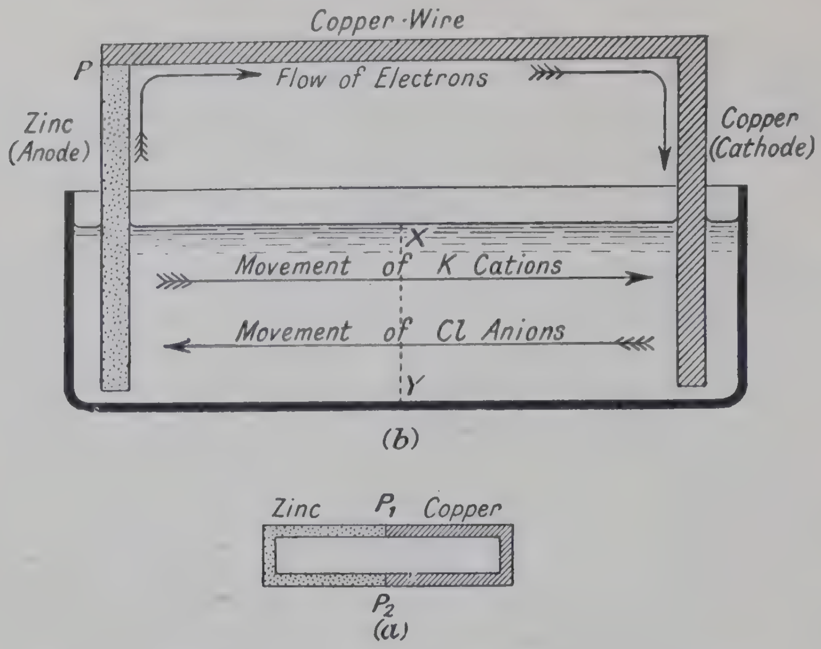

Fig. 1.—Movement of Ions and Electrons in a Circuit.

is the *cathode*.* The actual reactions at the boundaries between the liquid and metals will vary in different solutions, but in all cases they will provide for a continuous consumption of electrons at the copper surface, and a continuous supply of electrons at the zinc surface, so that the flow of electrons from the zinc to the copper, at the junction, P, will not result in an accumulation on one side or an exhaustion on the other; thus a flow of electricity through the metallic conductors can continue indefinitely.

Equilibrium Conditions

Reversible Cells. The cell described above, made by zinc and copper dipping into the same salt solution (potassium chloride), is not reversible; the reactions which occur when current passes through it in one direction are quite different from those which occur when current passes in the other direction. Certain cells containing two liquids are "reversible" in the sense that a small departure from equilibrium conditions in either direction causes a flow of current in one sense or the other, the same reactions taking place, although in opposite directions. The Daniell Cell, for instance, in which the copper is surrounded by copper sulphate solution and the zinc by zinc sulphate solution, with a porous partition separating the two liquids, is approximately reversible in that sense. Its E.M.F. may be obtained by balance on a potentiometer, a primitive form of which is shown in Fig. 2; a variable potential difference is applied to the cell by means of the sliding contact, S, and the slide is moved along the wire PQ (over which a potential gradient is applied from the cell C), until a position (X) is found at which the null galvanometer G shows no reading—which means that the E.M.F. of the cell is exactly equal to the potential difference between X and Q, and may be read off at once on the voltmeter V. In the case of a Daniell cell containing solutions of "normal" activity, balance will be obtained at about 1·11 volts; if a slightly lower P.D. is applied (say 1·10 volts), current passes through the cell in one direction, and if slightly more (say 1·12 volts), it flows in the other direction. In the first case metallic copper is deposited on the cathode, whilst zinc passes into the ionic state,

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* This definition of the anode and cathode as the poles towards which anions and cations respectively move applies both to current-producing and electrolytic (current-consuming) cells. Some confusion is often caused by the fact that the anode of a current-producing cell is the *negative* pole (i.e. the one which should be joined to the negative terminal of an ammeter), whereas, in an electrolytic cell, the anode is the *positive* electrode (i.e. the one which should be joined to the positive terminal of the dynamo or accumulator supplying the current).

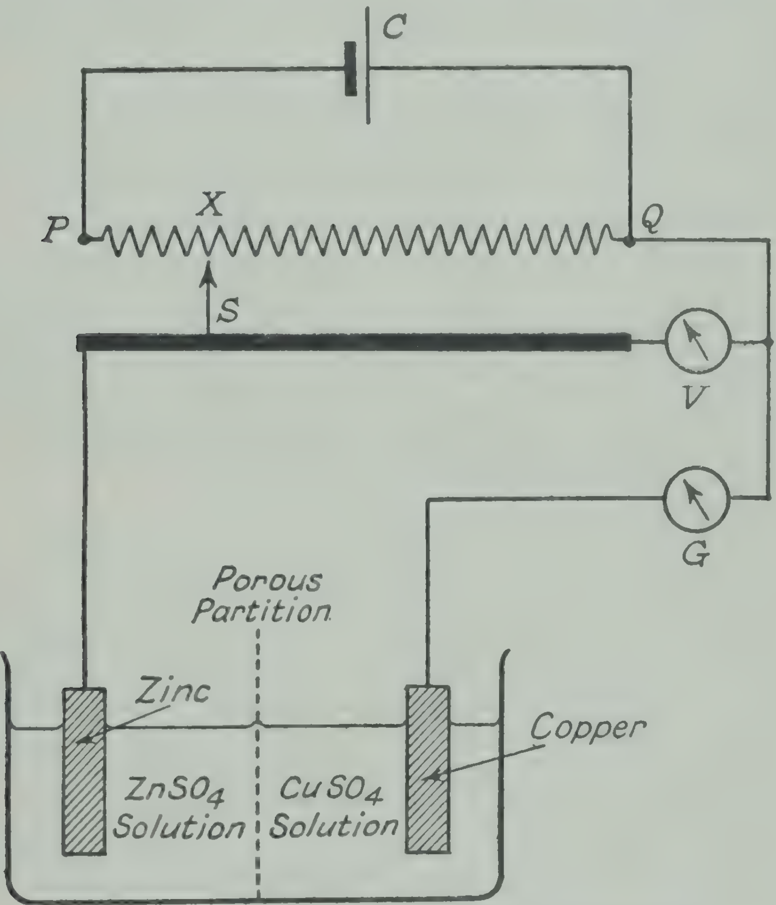

FIG. 2.—Daniell Cell and Simple Potentiometer.

$$Cu^{\cdot\cdot} + 2e = Cu$$
$$Zn = Zn^{\cdot\cdot} + 2e$$

In the second case, the same reactions occur in the opposite direction, metallic zinc being deposited and copper dissolved.

Instead of using copper and zinc, a cell of the "Daniell Type" may be made by immersing another pair of metals respectively in solutions of their salts. Any Daniell-type cell may be written in the general form

$$M_1 \mid M_1 \text{ Salt Solution} \mid M_2 \text{ Salt Solution} \mid M_2$$

Conception of a Half-Cell.[163] Cells of the Daniell type are, i general, approximately reversible, although the E.M.F.s which they ca balance vary greatly. Any such cell can be regarded as made up of tw half-cells

$$M_1 \mid M_1 \text{ Salt Solution}$$

and

$$M_2 \mid M_2 \text{ Salt Solution}$$

each of which contributes a characteristic P.D. (potential difference The value of the P.D. of any half-cell remains *unchanged*, irrespective o the nature of the other half-cell with which it is combined. The tota E.M.F. of the combination is equal to $E_1 - E_2$, where E_1 and E_2 are th P.D.s of the two half-cells.*

This fact was at one time taken to indicate that the E.M.F. of a galvani cell is associated solely with P.D.s occurring between the metal and th solution. Such a conclusion is now known to be incorrect. Frequentl much of the P.D. associated with a half-cell is located at the junctio between the electrode metal and the wire (usually copper) used to joi the half-cell to the potentiometer.† Nevertheless, if we include in ou definition of the half-cell a short piece of copper wire attached to metal M_1 or M_2 as the case may be, and consider the P.D. between the wire and the salt solution, the old conception of the E.M.F. of a Daniell type cell as the difference between the P.D.s of two half-cells may usefully be retained.

Normal Electrode Potentials. If we choose a certain half-cell as the arbitrary zero of a potential scale, we can assign a consistent value to the P.D. of any other half-cell. The *normal hydrogen electrode*, consisting of platinum covered with platinum black, and dipping into acid of normal hydrogen-ion activity (1·2 normal hydrochloric acid) saturated with hydrogen at 1 atmosphere pressure, has been adopted as arbitrary zero. The potential of the half-cell formed by any metal immersed in a solution of its salt of normal " cation activity " is called the *Normal Electrode Potential* of the metal in question.‡ A list of Normal Electrode Potentials on the *Hydrogen Scale* is given in Table I (Endpapers).

It is important to note that the normal electrode potential of a metal on the hydrogen scale really represents the E.M.F. needed to balance the cell formed by combining the normal electrode of the metal in question with the normal hydrogen electrode. The cell formed by joining a hydrogen electrode with a silver electrode is shown schematically in Fig. 3. If the P.D. between the acid surrounding the platinum and a point P on the copper wire joining the hydrogen electrode to the potentiometer is *adopted* as the zero of our arbitrary scale, then the potential difference between the liquid surrounding the silver electrode and a point Q on the copper wire joining it to the potentiometer will be given, *on the hydrogen scale*, by the potentiometer reading when balance has been obtained.

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* This expression neglects the P.D. at the junction of the two salt solutions—which may be made low if they are connected through a concentrated solution of a salt such as potassium chloride or ammonium nitrate, where both ions have almost the same mobility.

† The potential difference between copper wire and, say, the zinc plate of a Daniell cell will be the same whether the copper is in direct contact with the zinc, or whether a brass terminal is interposed.

‡ The " activity " of a dissolved substance is the " effective concentration " which (if adopted in the place of the actual concentration) would cause the Law of Mass Action to be obeyed. For dilute solutions it often differs little from the actual concentration. The exact evaluation of the activities of single ions presents difficulties.

As explained above, much of the potential drop is located at the junction between the metal and the copper wire, the rest being of course located between the metal and the solution. It would not affect the numbers given in Table I, if nickel wires were used in the place of copper wires; although this would shift the absolute value of the P.D. at the junction between wire and metal electrode, there would be a similar shift where the wire joined the platinum of the hydrogen electrode, and the measurement would remain unaltered. Similarly, any P.D. at the junction between the connecting wires and the alloy wire used for the windings of the potentiometer will not affect the numbers, since the P.D. at the entrance to the potentiometer will balance the P.D. at the exit.

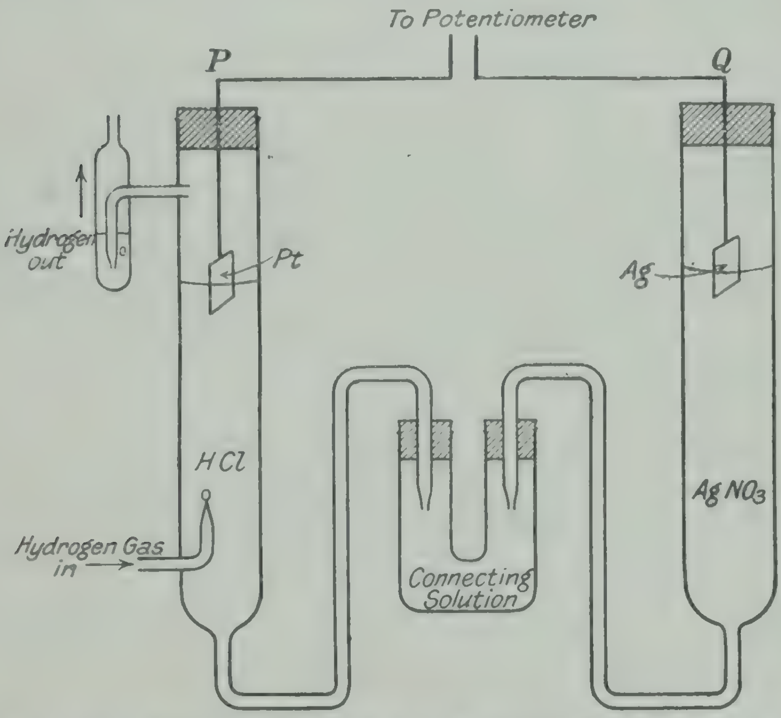

FIG. 3.—The Determination of the Electrode Potential of Silver.

Effect of Concentration. The normal hydrogen electrode consists of platinum immersed in acid of normal hydrogen ion activity saturated with hydrogen at one atmosphere pressure. It takes up the potential at which the passage of elementary hydrogen from the molecular state to the ionic is balanced by the passage from the ionic state to the molecular. An increase in the hydrogen pressure of the atmosphere, producing an increase in the concentration of molecular hydrogen, will favour the change in the first direction, but not in the second, thus up-setting the balance. A fresh balance may, however, be obtained at a mor negative potential. Thus an increase of hydrogen pressure above on atmosphere will render the potential negative, whilst a decrease wil render it positive, the change being expressed approximately by th equation

$$E_p = E_1 - \frac{RT}{2F} \log_e p$$

where E_p is the potential at pressure p atmospheres, E_1 the potential a one atmosphere, T the absolute temperature, R the gas constant, and F Faraday's Number.

Alternatively, keeping the gaseous pressure at one atmosphere, an increase of hydrogen ion activity in the liquid (i.e. an increase of concentration) will make the potential positive and a decrease negative. The equation is

$$E_c = E_1 + \frac{RT}{F} \log_e C = E_1 + \frac{2{\cdot}3RT}{F} \log_{10} C$$

where E_c is the potential at activity C, and E_1 the potential at normal activity of hydrogen ions. At 18° C., 2·3 RT/F is equal to 0·058 volts. The equation means, therefore, that, at a temperature of 18° C., in solutions where the activity can be regarded as equal to the concentration, the potential of the hydrogen electrode at one atmosphere pressure drops 0·058 volts every time the concentration is diminished to one-tenth of its previous value, as shown in Table II.

TABLE II

EQUILIBRIUM POTENTIAL OF HYDROGEN AT ATMOSPHERIC PRESSURE IN DIFFERENT LIQUIDS

Activity of Hydrogen Ions in Liquid	p_H Value	Example	Potential of Hydrogen-Saturated Platinum. Volts
Over 1·0 N	Negative	HCl above 1·2 N	Small Positive Values
1·000 N	0·000	1·2 N HCl	0·000 (*Arbitrary Zero*)
10^{-1} N	1	0·12 N HCl	− 0·058
10^{-2} N	2	0·011 N HCl	− 0·116
10^{-3} N	3	10^{-3} N HCl	− 0·174
10^{-4} N	4	10^{-4} N HCl	− 0·232
10^{-5} N	5	10^{-5} N HCl	− 0·290
10^{-6} N	6		− 0·348
10^{-7} N	7	Pure Water	− 0·406
10^{-8} N	8		− 0·464
10^{-9} N	9	10^{-5} N KOH	− 0·522
10^{-10} N	10	10^{-4} N KOH	− 0·580
10^{-11} N	11	10^{-3} N KOH	− 0·638
10^{-12} N	12	0·011 N KOH	− 0·696
10^{-13} N	13	0·12 N KOH	− 0·754
10^{-14} N	14	1·2 N KOH	− 0·812

The potential of the hydrogen electrode constitutes a convenient way of determining the hydrogen-ion activity of the liquid surrounding it. The so-called p_H scale is based on this. If the activity of hydrogen ions in a given liquid is 10^{-n}N, the p_H value of that liquid is said to be n. A neutral solution has a p_H value of 7·0, whereas acid solutions show lower values, and alkaline liquids higher ones. N/1000 hydrochloric acid with a hydrogen-ion activity of about 10^{-3}N will have a p_H value of about 3·0; N/1000 sodium hydroxide with a hydrogen-ion activity of about 10^{-11}N will have a value of about 11·0.

Amongst the numerous applications of this scale, one which is of special interest in corrosion problems is its use in denoting the character of natural waters. The acid waters of bog pools have low values (5·0 or even lower). Rainwater also is frequently acid. In London (Battersea Park) the p_H of rain was 5·0 in July 1936 but lower (3·9) in the following January, since coal (which contains sulphur) is burnt more freely in winter, so that the atmosphere contains more sulphur acids. In the country, higher values are obtained, especially in summer; at Godalming the value was 7·6 in July but 5·3 in January. In industrial towns where fumes are allowed to escape from chemical works, it may be much lower; at Burnley the value of rain was below 3·0 both in July 1936 and January 1937. The p_H value of the soil also varies, being usually low in moorland districts.

The potentials of the metals set out in Table I (Endpapers) are also altered if the activity (effective concentration) is not normal. Clearly, if the solution is diluted, the passage from the ionic to the metallic state will be slower, whereas the passage from the metal into solution remains unaltered. Thus the balance will be upset, but a fresh balance may be obtained at a more negative potential. The correction which must be applied is given by $\frac{RT}{nF}\log_e C$, where n is the valency. This means that at 18° C., if activity and concentration are regarded as identical, every tenfold dilution (say from N to N/10, or from N/10 to N/100) will shift the potential in a negative direction by about 0·058 volts for a monovalent ion, or 0·029 volts for a divalent ion. The theoretical shift of potential is approximately realized in the case of the more noble, and some of the less noble, metals; but in certain cases the potential actually measured is found to be almost independent of the concentration of the metallic salt in the original solution; this occurs if the metal is capable of reacting with the solution, so that the concentration in the layer next to the metal becomes different from that in the body of the liquid.

Effect of Films. The potentials given in Table I refer to metal free from an oxide film. Aluminium, which covers itself with an oxide film, highly protective and difficult to remove, commonly gives values much less negative than that indicated, so that aluminium is frequently "nobler" than zinc (i.e. it acts as the cathode of the cell Zn | Liquid | Al).

Effect of Complex-Forming Substances. Whilst oxide films on the metal tend to shift the potential in the positive (noble) direction, the presence of salts which form complex ions containing the metal in questio renders the potential abnormally negative. Thus copper placed in a solution containing cyanides may show values negative to hydrogen instea of the usual positive values; the cyanide ions combine with coppe ions, forming complex ions such as $[\mathrm{Cu(CN)_2}]'$ and locking up the bul of the metal in positions of low potential energy. The complex need no be an anion; in ammoniacal solutions, copper shows abnormally negativ potentials, due to complex cations such as $[\mathrm{Cu(NH_3)_4}]^{\bullet\bullet}$. If the comple provides a specially stable position for the copper atoms within the liquid the rate at which copper will be deposited on the metal will be slowe down, and equilibrium will only be obtained if the potential is shifted t a more negative value, so as to slow down the opposing passage from metal to liquid.

Potential in a Solution originally free from Ions of the Meta under Study. If a heavy metal is placed in a solution of some such sal as potassium chloride or sodium sulphate, the potential will tend to vary with time. Clearly, since the solution is initially free from ions of the metal in question, there can be no immediate equilibrium. Soon, however, owing to incipient corrosion, ions of that metal will begin to appear in the adjacent layers of the liquid. In general, a constant value of the potential will arise when some solid substance begins to separate out on the metallic surface, since the metal-ion concentration will then be kept constant at the saturation value. The solid may be either a salt or a hydroxide, and since the solubility of the solid body will be affected by the presence of a common anion in the solution, the value of the potential finally reached will be affected by the concentration of the potassium or sodium salt used, if the solid controlling the potential is a salt of the electrode metal; if, however, the solid is a hydroxide, the potential will depend on the $(\mathrm{OH})'$ concentration, that is on the p_{H} value (since the OH' concentration rises as the $\mathrm{H}^{\bullet}$ concentration falls). Thus Gatty and Spooner[64] found that the potential of lead in alkaline potassium chloride solution depended on the Cl' concentration if the ratio $\mathrm{Cl}'/\mathrm{OH}'$ exceeded $10^{5 \cdot 2}$, but on the p_{H} value if the ratio was less than that value. The potential of iron immersed in an aqueous solution originally free from iron ions depends on the hydrogen-ion concentration, becoming steadily more negative as the p_{H} value rises.

If solid silver chloride is stirred with potassium chloride of a certain concentration, the concentration of silver ions in the liquid will depend on the concentration of potassium chloride used. Thus a convenient standard electrode consists of silver surrounded by potassium chloride solution of known strength saturated with silver chloride. Similar standard electrodes can be based on mercury covered with various solutions saturated with mercurous salts. The well-known Calomel Electrode is one of these. The values of some standard electrodes on the hydrogen scale are given in Table III.

TABLE III

POTENTIALS OF SOME REFERENCE ELECTRODES

		Volts
Mercury	N KCl saturated with calomel (mercurous chloride) .	+ 0·281
Mercury	N/10 KCl saturated with calomel (mercurous chloride)	+ 0·334
Mercury	N H_2SO_4 saturated with mercurous sulphate . .	+ 0·682
Mercury	N/10 H_2SO_4 saturated with mercurous sulphate . .	+ 0·684
Mercury	N NaOH saturated with mercuric oxide . . .	+ 0·114
Mercury	N/10 NaOH saturated with mercuric oxide . .	+ 0·169
Silver	N/10 KCl saturated with silver chloride . . .	+ 0·289

Determination of Electrode Potentials. It would be possible to determine the normal electrode potential of any metal (say silver) by placing it in a solution of a salt (say the nitrate) of normal activity, joining it to a normal hydrogen electrode through a connecting solution chosen to suppress liquid junction potentials (Fig. 3, p. xxvii), and measuring on a potentiometer the potential needed to balance the E.M.F. of the combination. The value (0·799 volt for silver) will represent the normal electrode potential of silver on the normal hydrogen scale.

In such cases, however, it is often easier to substitute for the hydrogen electrode a standard half-cell such as a calomel electrode, and measure the balance potential of the combination.

Ag | $AgNO_3$ (normal activity) | Connecting Solution (say concentrated NH_4NO_3) | Normal KCl | Hg_2Cl_2 | Hg

By " adding " to the value obtained experimentally (say + 0·518 volt) the value of the calomel half-cell on the normal hydrogen scale (+ 0·281 volt), we get the value for silver on the hydrogen scale

$$0{\cdot}518 + 0{\cdot}281 = +\,0{\cdot}799 \text{ volt.}$$

It will be noted that for a base metal, which would have a potential strongly negative to calomel, the effect of this " addition " would be to *decrease* the numerical value.

The Calomel (or Silver Chloride) Electrodes are useful in other ways. If (Fig. 4) the open tip of a tubulus leading to such an electrode is brought up against a selected point (P) on a metal surface immersed in a solution, the value of the reading between the standard electrode and the metal will be affected by " corrosion currents " passing to or from the metal at the point in question ; the reading is displaced in one direction if the point is cathodic, and in the other if it is anodic, by an amount depending on the current density. If the relation between the potential reading and the cathodic or anodic current density has previously been determined by independent measurements on specimens to which known currents have been applied, it is possible to obtain a measure of the current density at any point on the corroding specimen, without actually tapping the current. Alternatively by moving the tip of the tubulus in turn to different points in the liquid near the metallic surface, and by taking readings at each point, the distribution of potential in the liquid may

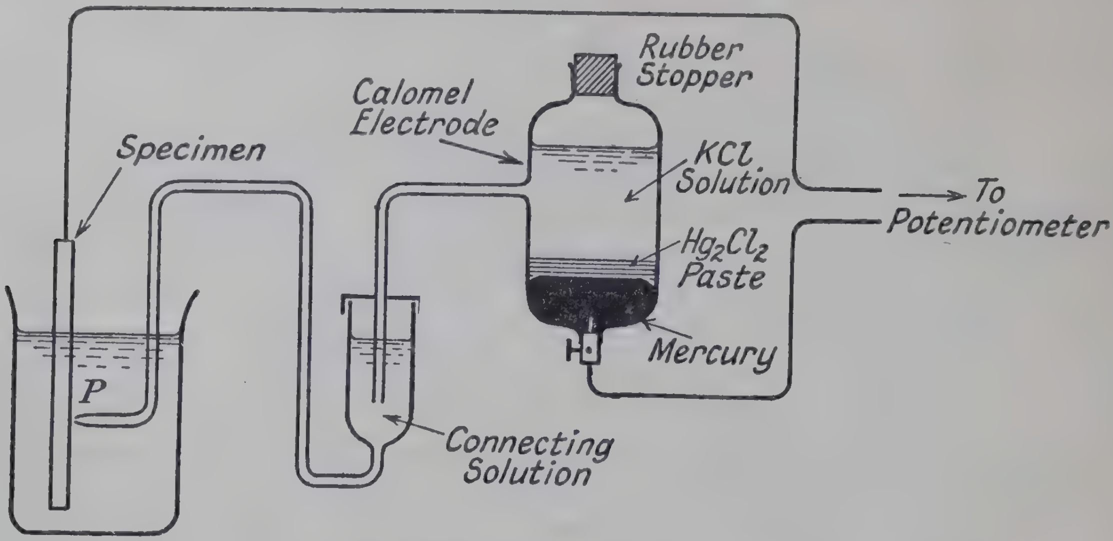

FIG. 4.—The Calomel Electrode used for measuring a local P.D.

be studied, which will also serve to furnish a measure of the currents flowing. These two methods have been used at Cambridge by Hoar [52] and Agar [1] respectively in their estimations of corrosion currents (see pp. 34, 36).

Non-equilibrium Conditions

Polarization. The potentials recorded in Tables I and II represent equilibrium values. In order that a metal shall suffer anodic attack, the potential must be moved slightly in the positive direction ; if cathodic deposition is to take place upon it, the potential must be moved in a negative direction. These shifts of potential are known as anodic and cathodic " polarization " respectively. For metals like silver, the shift from the equilibrium value is small even when a moderate current is flowing. It is mainly connected with " concentration polarization " ; around a dissolving anode the concentration of cations increases, which would tend to raise the potential even if the current ceased to flow ; similarly, at a cathode deposition leaves the solution locally impoverished of cations, which would produce a shift in the negative direction.

Overpotential of Metallic Deposition. In a few cases the changes are much more serious. On iron and nickel, cathodic deposition only becomes appreciable if the potential is made considerably more negative than the equilibrium value, whilst dissolution only becomes important if it is moved appreciably in the opposite direction. This irreversibility of iron stands in contrast to the behaviour of silver, where a very small increase of potential from the equilibrium value will produce anodic attack, and a very small shift in the negative direction will produce cathodic deposition. The difference between the two cases has been explained in different ways. Some attribute it to the fact that the crystal lattice of metallic silver contains silver ions " ready-made ", so that the passage of silver to or from the solution to the metal occurs smoothly. In iron, ions probably do not exist ready-made in the same sense, and a definite "overpotential", or departure from the equilibrium value, must be applied before sensible dissolution or deposition occurs. The difference can be seen in another way; silver deposited from a silver nitrate solution on a cathode yields a limited number of big crystals, since, wherever a crystal nucleus already exists, the silver atoms will arrange themselves readily so as to convert the small crystal into a big one. Iron or nickel, however, instead of forming a limited number of big crystals, produce deposits on the cathode consisting of a large number of small crystals. Thus smooth, fine-grained deposits can be obtained from a solution of a simple salt of nickel, whereas a simple salt of silver yields rugged deposits; as shown below, smooth deposits of silver are obtainable from baths containing complex salts.

Effect of Complex Salts. A solution of a complex cyanide, such as $K\,Ag(CN)_2$, $K\,Cu(CN)_2$ or $K_2\,Zn(CN)_4$, contains complex anions $[Ag(CN)_2]'$, $[Cu(CN)_2]'$ or $Zn(CN)_4]''$, and, as explained on p. xxx, metals show abnormal potentials in such solutions. For instance, when the ordinary Daniell cell

Cu | $CuSO_4$ solution | $ZnSO_4$ solution | Zn

furnishes current, the zinc is the anode and passes into solution, whilst the copper is cathode, fresh metal being deposited on it. On the other hand, the cell

Cu | KCN solution | $ZnSO_4$ solution | Zn

furnishes a current in the opposite direction, the copper being the anode. Similarly, although tin is cathodic to iron in most salt solutions, it becomes anodic to iron in certain organic acids, because the tin becomes locked up as complex anions (see p. 165).

Complex salt solutions are often used for electroplating, especially for coating articles of complicated geometrical shape, which, if plated in a simple salt solution, receive much deposit on the prominent parts, the recesses being neglected. If a complex salt solution is used, with most of the metal locked up as complexes of great stability, it is impossible to cause rapid deposition at the prominent parts, because polarization sets in, the potential being altered in such a manner that deposition is diverted to the recesses; these solutions are said to have good *throwing power.*

The same complex ion solutions often provide smooth coats where simple salt solutions would give rugged macrocrystalline deposits. The explanation may be similar to that of the improved throwing power, but it is generally supposed that the main cause of the smooth deposits obtained from cyanide baths is the adsorption of the cyanide as a "poison" on the tips of the crystals, where growth would otherwise proceed; this favours the production of new small crystals instead of the growth of the original large ones. Colloids—organic bodies like gelatine as well as metallic hydroxides—are also added to give smooth bright deposits (see p. 153).

Overpotential of Hydrogen Evolution. Very important in corrosion is the overpotential attending the cathodic liberation of hydrogen. The potential needed for the liberation of hydrogen must be made more negative than the equilibrium value, by an amount which depends both on the metal forming the cathode, and also the current density passing, as indicated in Table IV. For most metals, the relation between the over-potential (η) and current density (i) is given by

$$\eta = a + b \log i$$

where a and b are constants.

The cause of overpotential has been the subject of much discussion. The formation of hydrogen at a cathode consists of two main stages :—

(1) The combination of a (hydrated) hydrogen ion with an electron to give a hydrogen atom (water being liberated).

(2) The combination of two hydrogen atoms to give a hydrogen molecule.

Evidently on metals of high overpotential, one or both of these reactions must work "stickily". Opinion is still divided as to the respective responsibilities of the two stages for the obstruction ; probably either may control the situation in different cases. From the point of view of corrosion, it is very important to decide the responsibility of each stage. If overpotential were wholly due to impedance with the first stage, it would be beneficial, since it would reduce the amount of hydrogen formed

TABLE IV*

Current Density	Current just sufficient for Bubbles		1 amp./dm.		10 amp./dm.	
Authority	Caspari	Thiel	Tafel	Knobel	Tafel	Knobel
Mercury	0·78	0·57	1·17	1·04	1·30	1·07
Zinc	0·70	0·48†	—	0·75	—	1·06
Lead	0·64	0·40	1·09	1·09	1·23	1·18
Cadmium	0·48	0·39	1·11	1·13	1·22	1·22
Tin	0·53	0·40	0·98	1·08	1·15	1·22
Bismuth	—	0·39	0·88	1·05	1·00	1·14
Aluminium	—	0·30	—	0·83	—	1·00
Graphite	—	0·33	—	0·78	—	0·98
Carbon	—	0·14	—	0·70	—	0·89
Copper	0·23	0·19	0·58	0·58	0·79	0·85
Nickel	0·21	0·14	0·56	0·75	0·74	1·05
Silver	0·15	0·10	—	0·76	0·93	0·88
Iron	—	0·17‡	—	0·56	—	0·82
Palladium	—	0·00	—	0·30	—	0·70
Gold	0·02	0·02	0·74	0·39	0·95	0·59
Smooth Platinum	—	0·08	—	0·07	0·5	0·29
Platinized Platinum	0·005	0·00	0·04	0·03	0·07	0·04

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* Largely based on A. J. Allmand and H. J. T. Ellingham, "Principles of Applied Electrochemistry" (Arnold), 1924, p. 89.

† In 0·01 M zinc acetate.

‡ In 0·1 M sulphuric acid saturated with ferrous sulphate.

at a cathode, and would generally reduce the velocity of corrosion. Impedance of the second stage may, however, be disastrous, since this will not prevent the formation of atomic hydrogen within the metal, but will merely prevent its evolution in (molecular) gaseous form at the external surface of the metal. Since atomic hydrogen can diffuse rapidly through many metals, such as iron and aluminium, the effect may be serious. In the case of iron, hydrogen absorbed into the metal may be evolved, internally, particularly at rifts or cavities associated with inclusions, and, producing there gaseous (molecular) hydrogen under high pressure, may lead to blistering or embrittlement (see p. 111).

The overpotential of hydrogen evolution can be made very low by using a platinum cathode, and is reduced still further if the platinum is "platinized" (i.e. covered with platinum black)—which increases the effective area.

The Oxygen Electrode. Overpotential is more difficult to eliminate on an oxygen electrode than on a hydrogen electrode. If the oxygen electrode behaved reversibly, the equilibrium

$$O_2 + 2H_2O + 4e \rightleftharpoons 4(OH)'$$

should be reached at a potential 1·23 volts above that of the reversible hydrogen electrode in the same liquid. Actually, to produce free oxygen in an electrolytic cell fitted with a platinum anode requires a potential far *higher* than the reversible value. Conversely, when an attempt is made to use platinum surrounded by a liquid saturated with oxygen as the cathode of a current-producing cell, potentials far *lower* than the theoretical value are obtained. Thus the oxygen electrode is highly irreversible.

The matter has largely been cleared up by Hoar,[78] who finds that, although equilibrium between a platinum electrode and an oxygen-saturated electrode is never obtained at the reversible potential, a very small anodic current density is sufficient to bring the potential to the reversible value; the amount of the current needed to keep the potential at that value decreases steadily with time. Apparently the platinum is covered with a porous oxide film, and the current flows between the film surface as cathode and the metal exposed at the pores as anode, causing an irreversible consumption of electromotively active oxygen at the film surface; since there is no corresponding consumption of the O'' or OH' ions, equilibrium must be upset, leading to a lowering of the potential registered. It is possible to maintain the reversible potential on the platinum, provided that a small current is applied, equal and opposite to that flowing down the pores. As the film grows thicker, the resistance of the electrolyte path through the pores increases, and the strength of the current required to maintain the potential at the reversible value falls off.*

At anodic or cathodic current densities large compared to the leakage current, Hoar's curves indicate that the logarithm of the current density plotted against the potential is a straight line. The two straight lines for the anodic and cathodic curves, when produced, cut at about the reversible potential, indicating that, if the irreversible effect due to film-leakage were not present, the two changes would balance one another at or near the theoretical value.

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* Alternatively, the electromotively active oxygen may be continuously removed at a slow rate by a general thickening of the oxide layer produced by the migration of platinum ions outwards through the film (T. P. Hoar, unpublished work).

If in the place of platinum, a base metal electrode is immersed in a liquid saturated with oxygen, the potential will be far below the equilibrium value of the oxygen electrode, and usually not very much above that of the film-free metal. The potential measured will rise as the film becomes more and more free from pores, but, for an oxide film in a given state of repair, it will be higher when the oxygen concentration of the liquid is high than when the concentration is low.* The fact that a metal immersed in oxygen-rich liquid has a higher potential than the same metal in oxygen-poor liquid is of considerable importance, being the cause of *Differential Aeration Currents* (p. 27).

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* The graphical method of p. 68 is useful in explaining the effect of (1) the state of film repair, (2) the oxygen concentration.

AN INTRODUCTION TO METALLIC CORROSION

Chapter I

FILM GROWTH

General

Classification. The word " Corrosion " will be used in this book to cover all transformations in which a metal passes from the elementary to the combined condition ; it will include reactions leading to a solid crust of oxide or sulphide, and also those resulting in a clear solution of chloride or sulphate, although here evaporation is needed to isolate the compound in the solid state. Whether this is the accepted use of the term " Corrosion " matters little ; there is no other English word capable of describing the subject of the book, and it is probably better to adapt an existing word than to coin a new one.

Corrosion changes may be divided into two classes : those which produce a solid film and those which do not. Film-forming reactions usually become increasingly slow as the film thickens, whereas, in the absence of film-formation, the velocity of attack is unlikely to slow down with time, except as a result of the exhaustion of a reactant.

The present chapter is concerned with film-forming reactions. The fact that such reactions often choke themselves is important, because it explains why metals exposed to the atmosphere generally escape destruction. The observation that bright iron can be exposed to reasonably dry air without visible change might suggest that iron has little affinity for oxygen, but measurements of free energy show that actually the affinity s high. The true cause is different. If an oxide-free surface of iron is exposed to dry air, there is rapid combination, but as soon as the growing oxide film begins to isolate the metal from the air, oxidation becomes slow, although it does not cease entirely. Vernon [151] found that, even after some weeks exposure to air, iron was still slowly increasing in weight.

Action of Iodine on Metals. The difference between filming and non-filming reactions can be illustrated by the observations of Parsons [116] on metals introduced into solutions of iodine in various organic liquids. Whenever he used a solvent capable of dissolving the iodide of the metal under examination, the metal passed into solution without hindrance as ts iodide. But whenever the solvent was one which left a layer of solid odide undissolved on the metallic surface, there was little attack, since he layer shut off the two reacting elements from one another.

Later work showed that even where a solid layer is formed, blockage of the attack may not be immediate ; film growth may begin rapidly becoming slow as the film thickens, as found by Bannister [51] in th author's laboratory during a detailed study of film growth on silver expose to a chloroform solution of iodine. Some of the curves are reproduce in Fig. 5. Their analysis shows that, over a considerable range of thickness, the rate of thickening is inversely proportional to the thicknes attained. Thus if y is the thickness reached in time t

$$dy/dt = k/y$$

where k is a constant. The equation may also be written

$$y^2 = \mathrm{K}t + \mathrm{K}'$$

where K represents $2k$, and K′ is the integration constant. This sam "parabolic" relationship had previously been found by Tammann [13] for the action of vaporous iodine on metals.

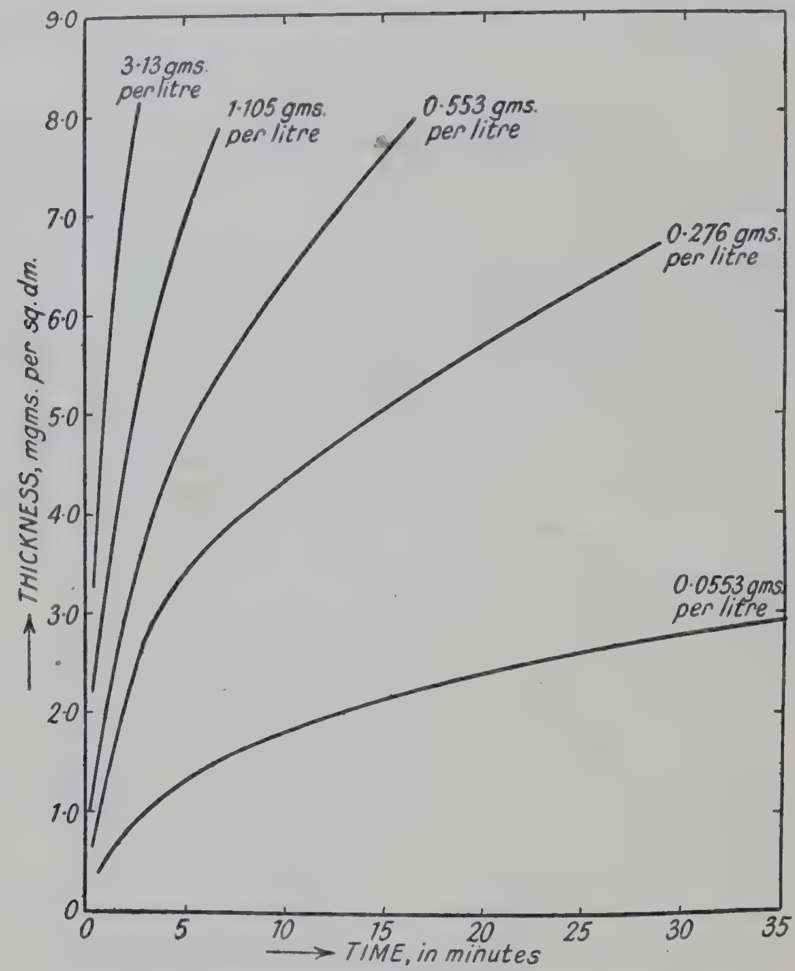

Fig. 5.—Growth of Iodide on Silver (U. R. Evans and L. C. Bannister).

Such an equation is in no way surprising ; the rate of the passage o heat through a plate is inversely proportional to the thickness, and it i reasonable to expect the passage of matter through a film to be inversel proportional to the thickness also, whether the metal moves outward through the film or the iodine inwards. The manner in which the curve re influenced by the iodine concentration in the liquid rather suggests hat, in this case, the non-metal moves inwards; but in the high-emperature oxidation of metals (p. 15), the metal certainly moves outwards to meet the oxygen—not vice versa.

If the equation $dy/dt = k/y$ were obeyed from the outset, it would mply an infinite growth rate when y was zero, that is before any film had ppeared. Now chemical considerations would preclude an infinite eaction velocity; even in a liquid where no film is formed, corrosion loes not proceed infinitely fast. Hence there must be a departure from he relationship in the early stages. Bannister found that the parabolic aw was not obeyed at the outset, when the iodide films were very thin.

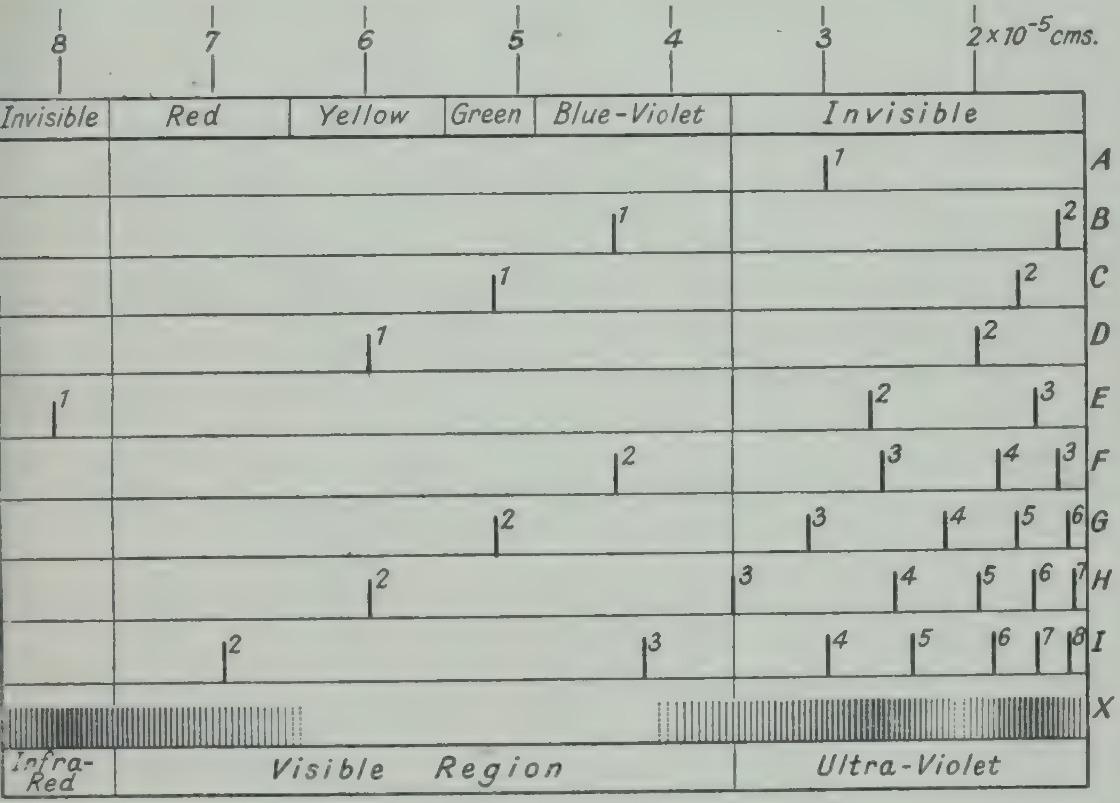

FIG. 6.—Production of Interference Tints.

Interference Tints. Iodide films on silver produce a beautiful series of colours, due to interference between light reflected from the outer and inner film-surfaces. Interference may be expected whenever the effective paths travelled by the light reflected at the two surfaces differ by an odd number of half wave-lengths. Consider a film being formed on a metallic surface, which is viewed by white light. As long as the film is very thin, the interference band will be in the ultra-violet (Fig. 6 (A)) and there will be no colour. When a certain thickness (usually between 200 and 400 Å according to the film substance) is reached, the blue light reflected at the outer surface will be out of phase with that reflected at the inner surface (Fig. 6 (B)); partial extinction of the blue waves will make the surface appear yellow. When a greater film thickness is reached, the longer green waves suffer interference (C), producing a mauve colour; a still greater thickness causes interference of yellow light, leaving the reflection blue. Since interference can again

TABLE V

	Colours produced by Air-films between Glass (" Newton's Rings ")		Colours produced by Films on Metals		
Order	Viewed by Reflected Light	Viewed by Transmitted Light	Oxide-films on Lead or Nickel. Iodide-films on Silver. Hydroxide-films on Aluminium	Oxide-films on Iron	Oxide- or Sulphide-films on Copper
" Invisible Range."	Colourless (black).	Colourless (white).	Colour of metal unchanged.	Colour of iron unchanged.	Colour of Copper unchanged.
First order.	Blue.	Yellow.	Yellow to brown	Yellow to brown.	Brown.
	Faint green.	Red to mauve.	Rose to mauve.	Mauve.	Rose to mauve
	Yellow.	Blue.	Blue.	Blue.	Blue.
	Red.	Green.	Silvery (greenish, if film is imperfect).	Silver grey.	Brilliant silver (occasionally greenish).
Second order.	Blue.	Yellow.	Yellow to brown	—	Yellow-brown *
	Green.	Red.	Red.	Pinkish blue.	Red.
	Yellow.	Blue.	Blue.	Blue.	Blue.
	Red.	Green.	Green.	Greenish blue.	Green.
Third order.	Blue.	Yellow.	Yellow.	—	Brown.
	Green.	Red.	Red.	Bluish grey (with trace of pink).	Red.
	Yellow.	Greyish blue.	(Trace of Lavender blue.)	Bluish grey (specific colour).	(Trace of Lavender blue).
	Red.	Green.	Green.	,,	Green.
Fourth order.	—	Dull yellow.	—	,,	—
	Green.	Red.	Red.	,,†	Dirty red.
	Red.	Green.	Green.	,,	Dirty green.
Fifth order.	Greenish.	Red.‡	Faint red passing into specific colour of film-substance.	,,	Grey (sometimes trace of red).

* To obtain the higher-order colours on copper, mildly oxidizing conditions are needed, otherwise the colour (due to cuprous oxide) is hidden by sooty cupric oxide.

† If the films are produced carefully, the fourth-order red can be seen on oxidized iron.

‡ Further alternations of red and green can usually be made out, representing sixth- and seventh-order colours.

occur when the path-difference reaches 3/2, 5/2, 7/2 or 9/2 times the wave-length of the light in question, various orders of colours are possible; silver iodide films exhibit five orders, red appearing five times. The sequence, shown in Table V, is not a simple repetition, since the various absorption bands will follow one another across the spectrum at unequal intervals,* as shown in Fig. 6. The first-order colours are produced as the first band (marked 1) passes across the visible part of the spectrum (B, C and D). If the bands are narrow (as is usually the case for films on brightly reflecting metal, provided the thickness is fairly uniform), the first band will have passed out into the invisible infra-red before the second has entered from the invisible ultra-violet (Fig. 6 (E)); thus on metals there is a silvery hiatus between the first- and second-order colours.† The second-order yellow, red and blue appear when the second band is in the positions shown in (F), (G) and (H). The third band follows more closely on the second than the second follows on the first, and must enter the visible region before the second has left, so that there is always a green at the end of the second order (Fig. 6 (I)).

Oxide films produced on heating nickel in air (and hydroxide films formed on aluminium in the early stages of corrosion by salt solution) produce almost the same colour sequence as iodide films on silver (Table V). The films on heated iron consist of ferric oxide, a less transparent substance, and the later colours, corresponding to the thickest films, are weak or missing; on copper heated to give cuprous oxide films, the early colours are modified somewhat by the colour of the metal, whilst the later ones are apt to be obscured by sooty specks of cupric oxide on the outer surface, unless the atmosphere used to oxidize the copper has contained so little oxygen as to make the formation of cupric oxide impossible.

If nickel oxide films are transferred from the nickel basis to a transparent support (e.g. a plate of celluloid), the colour shown by any particular film by reflected light is complementary to that shown by the same film on the metal—as would be expected on optical principles. The relation is presented in Table VI. In the case of the thinner ferric oxide films (which rest directly on iron), the same complementary relation is obtained. The thicker films on iron have a layer of opaque magnetite interposed between ferric oxide and metal and do not show the complementary relation. If viewed through the celluloid, the colour is the same as that shown before the removal of the metallic iron, since the reflecting basis (magnetite) remains the same as before; if viewed from the other side (where metal had existed before the transfer) no colours can be seen, since the dark grey magnetite layer hides the films (Fig. 7).

---

* For a film of effective thickness y and refractive index n, the centres of the absorption bands will fall at wave-lengths $4ny$, $4ny/3$, $4ny/5$, $4ny/7$, . . . etc.

† In contrast, the bands produced by air films (e.g. those responsible for Newton's rings viewed by *transmitted* light, which furnish a colour sequence similar to that given by films on metals viewed by *reflected* light) are much broader; the first band may still cause absorption in the red after the second has entered the blue (Fig. 6 (X)), and consequently a green appears at the end of the first order.

TABLE VI

Colours produced by Oxide Films (Reflected Light) before and after Transfer (U. R. Evans)

Nickel		Iron	
Colour on Metal	Colour after Transfer	Colour on Metal	Colour after Transfer
Yellow I	Bluish white	Yellow or brown	Bluish silver
Mauve I	Whitish	Mauve or violet	Silvery grey (sometimes faintly green)
Blue I	Yellow		
" Silvery hiatus "	Red	Full blue	Golden yellow
Yellow II	Mauve to blue	Pale blue	Reddish
Red II	Green	Pinkish blue	Colours when viewed through plastic unchanged; from back, colours hidden by magnetite layer
Blue II	Yellow	Blue	
Green II	Red	Greenish blue	
Red III	Green	Bluish grey with trace of pink	

The method developed by the author [43] for transferring the films consists in cementing the celluloid plate with celluloid solution to the film-covered face of a rectangular sheet of iron or nickel, which is then fixed in the electrolytic vessel (Fig. 8) and joined through resistances to the positive pole of a battery, so as to remove the metal by anodic corrosion, leaving the film on the celluloid; the removal should start from the lower end of the rectangle and spread steadily upwards without leaving

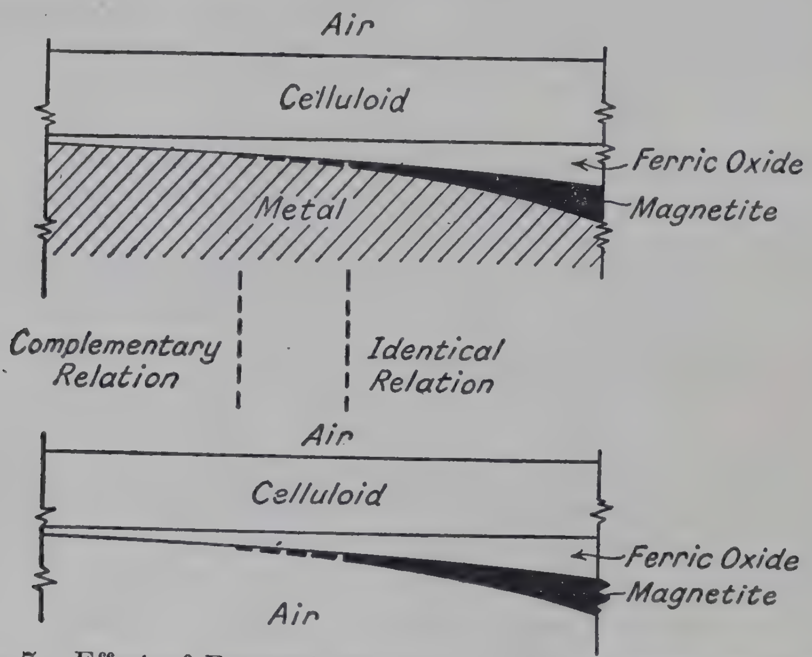
Air
Celluloid
Ferric Oxide
Metal
Magnetite
Complementary Relation
Identical Relation
Air
Celluloid
Ferric Oxide
Magnetite
Air

Fig. 7.—Effect of Removal of Metal on Colours shown by Films.

uncorroded "islands" of metal, since any portion which ceases to be connected with the external battery will fail to be removed. The solution employed contains sodium chloride along with zinc sulphate, which is added so that the cathodic reaction shall be the deposition of zinc and not the production of alkali. In the case of iron, it is necessary to ensure a high anodic current density along the line where the oxide, metal and solution meet, so as to avoid the cathodic destruction of the film by means of the local cell

Iron | Solution | Ferric Oxide

(see p. 42). The peculiar geometrical form of the vessel adopted (Fig. 8) is designed to fulfil these requirements.

Measurement of Thickness of Films. The simplest method (in principle) for obtaining the mean thickness of a film of oxide, sulphide or iodide is to weigh the metal before and after the surface has been converted into oxide, sulphide or iodide; the difference in weight represents the non-metal taken up.* If an oxide film is already present at the first weighing, the difference will not represent the total oxide present after the second weighing, and to avoid this error Gulbransen [69] has designed a special balance in which specimens can be ignited in hydrogen before the first weighing. The gravimetric method was used in Pilling and Bedworth's classical work [120] on high-temperature oxidation, whilst Vernon [147] has used it in refined form to follow film growth at ordinary temperatures in various atmospheres. Bannister's curves for the growth of silver iodide films [51] (Fig. 5, p. 2) depended directly or indirectly on microbalance measurements.

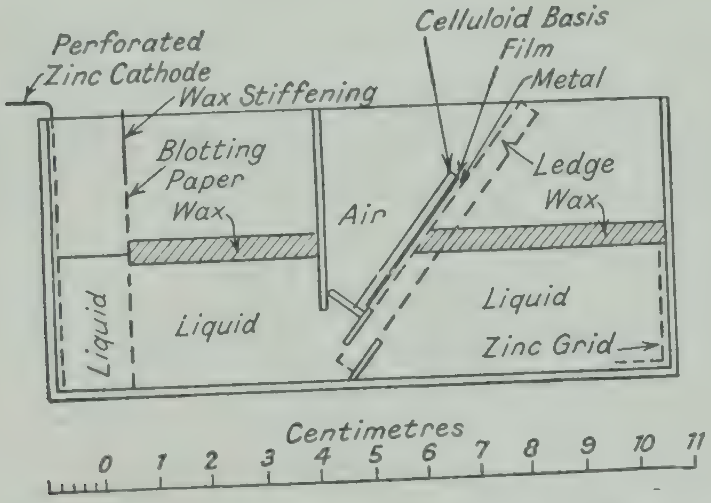

FIG. 8.—Cell designed for Transfer of Oxide Films to Celluloid.

Another method, which has given good results in the hands of Vernon, Wormwell and Nurse,[156] is to strip oxide films from iron by dissolving the metal in a dry methyl-alcoholic solution of iodine, and then to estimate the iron in the films thus isolated.

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* If the weight increase on area A is W, the film thickness is $WM/(M - m)DA$ where D is the density of the film substance, M its molecular weight and m the weight of metal in the molecule.

A third method depends on the change in the ellipticity of polarized light reflected at a metallic surface—which change is modified by the presence of a film to an extent depending on the thickness. For details of this beautiful method, reference must be made to the papers of Tronstad [144] and Winterbottom.[164] In the form used by these investigators, the method is suitable for measuring invisible films too thin to give interference tints; in Mehl's laboratory the principle has been developed by Leberknight,[97] Lustman[100] and others for the measurement of thicker films.

Tammann,[138] in his classical work on film growth, used a simpler method to obtain the thickness; he turned to the Tables showing Newton's ring colours as observed by *transmitted light* to find the thickness of the air film which gave a colour matching that of the film-covered metal; he divided this figure by the refractive index of the film substance and obtained thereby an estimate of the film on the metal. This delightfully simple plan of obtaining measure without measurement involves, however, certain inaccuracies, and it is well to calibrate the colour scale of thickness by measuring the thicknesses of films corresponding to different tints by some alternative method—a procedure adopted by Bannister. Another accurate procedure has been described by Constable,[24] who used a spectrometer to obtain the wave-lengths corresponding to the centres of interference bands, and thus calculated the film thicknesses.

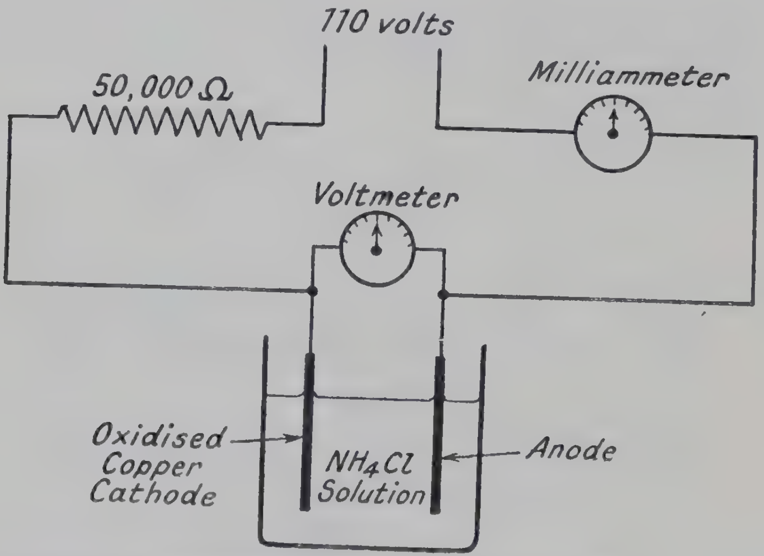

FIG. 9.—Electrometric Estimation of Oxide Films (H. A. Miley and U. R. Evans).

The electrometric method, used in a simple form by Bannister in studying iodide films, was later developed for oxide films in the author's laboratory by Miley [54] and further improved at New York by Campbell and Thomas.[18] In Miley's procedure, the film-covered specimen (Fig. 9) is made the cathode in a solution of ammonium chloride, the current being furnished by a high E.M.F. passing through a high series resistance, so that its strength remains unaffected by any resistance-changes or olarization-changes occurring in the cell. A voltmeter or potentiometer laced in parallel shows a rise when the reduction of the oxide is complete, ince a larger potential drop is needed to evolve hydrogen than to reduce xide; from the number of coulombs needed for reduction, the film hickness can be calculated.* Cuprous oxide films are reduced to metallic opper, ferric oxide to the ferrous state which permits immediate dissolu- ion in the ammonium chloride solution; the method is only suited for ilms which can be reduced without evolution of hydrogen. The end- oint is fairly sharp in cases where there is a sharp boundary between film nd metal, but vague where there is interlocking.

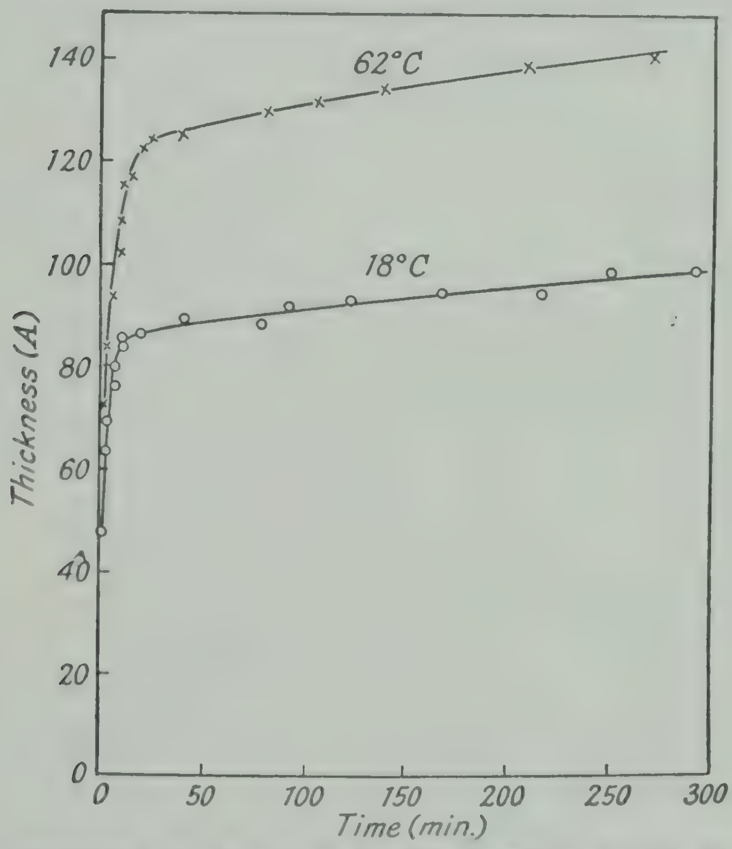

Fig. 10.—Oxidation of Copper in Air (H. A. Miley and U. R. Evans).

Comparisons between the results of the different methods of measure- ent have been carried out at Cambridge. Wherever possible a single pecimen has been used for all determinations, since two or more speci- ens, nominally identical, may not behave alike when treated in the same ay. Bannister exposed weighed silver specimens in iodine solution, nd then reweighed them; the weight increment enabled one value or the thickness of the iodide film to be calculated. He then determined he coulombs needed for the cathodic reduction of the film, obtaining a econd measurement, and finally estimated the iodine which had passed into solution; this provided a third figure. Thus three measurements were obtained from each individual specimen, and, since all three were generally in good accord, confidence was felt in all three methods of estimation.

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* If reduction is complete in time t, using current I and a specimen of area A, the ickness of the film is ItJ/FAD, where J is the equivalent weight of the oxide (for the ppropriate reaction), D its density and F Faraday's number.

Similarly Price and Thomas [124] took weighed specimens of silver, and formed a film of sulphide on each, the gain in weight furnishing one measure of the thickness; the number of coulombs needed to reduce the film provided a second and the accompanying loss of weight a third. Here again, there were three measurements from a single specimen, and reasonable accord was obtained.

The comparisons between the thicknesses of oxide films corresponding to a given colour, obtained by different experimenters using different methods, have not always shown such good agreement, although the order of magnitude is not in doubt. There are several reasons for the discrepancies, one being that two metal specimens tinted to the same colour but differing in previous history, may carry different amounts of oxide per unit area, as shown by Vernon and his colleagues; [156] this may happen if the original grinding of one has been more vigorous than the other, since isolated masses of oxide pushed down below the surface may not appreciably affect the colour produced when subsequently a uniform film is formed over the surface by heating in air.

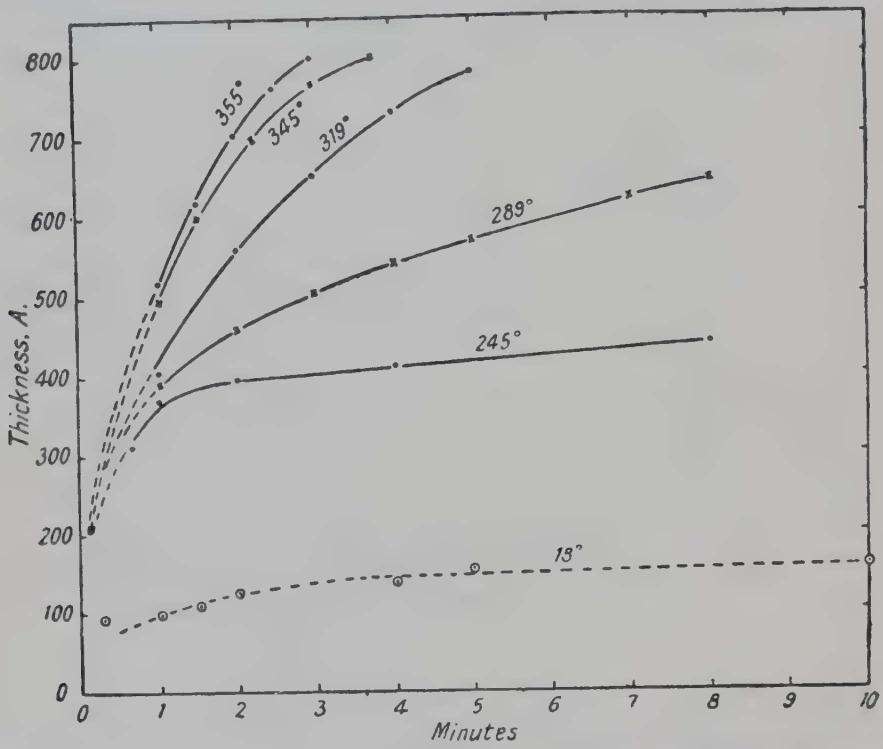

FIG. 11.—Oxidation of Iron in Air (H. A. Miley and U. R. Evans).

Mechanism of Oxidation

Time-Oxidation Curves. By exposing freshly abraded specimens of copper and iron to dry air for different times, and measuring the oxide film electrometrically, Miley obtained curves representing the progress of oxidation (Figs. 10 and 11). These show clearly that even at ordinary temperatures the oxidation is very rapid in the opening stages, but soon slows down as the film begins to isolate metal and air from one another. The oxidation at ordinary temperatures produces no change in the appearance of the metal (unless sulphur compounds are present in the air). At higher temperatures, the film quickly becomes sufficiently thick and sufficiently regular to give interference tints, but even in such cases the rate of thickening falls off as the film becomes thicker.

The curves obtained by gravimetric methods present the same general features. Fig. 12 reproduces some of the results of Vernon, Akeroyd and Stroud [153] on the oxidation of zinc.

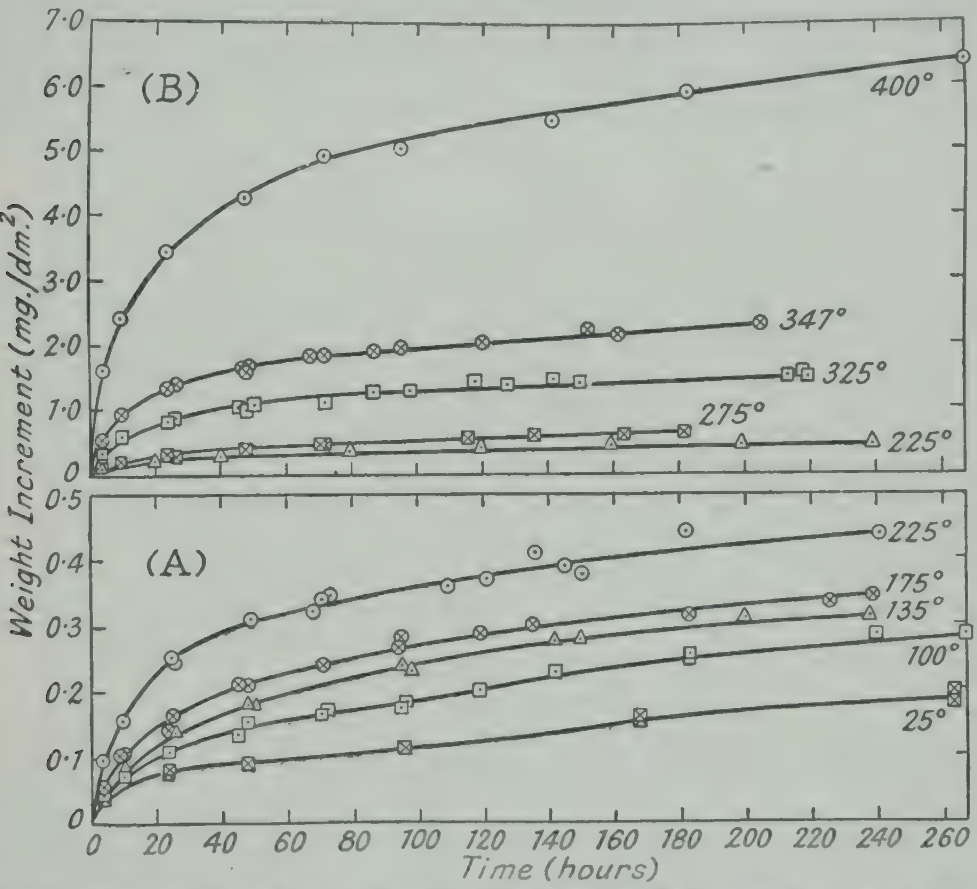

FIG. 12.—Oxidation of Abraded Zinc exposed to Air at Different Temperatures (W. H. J. Vernon, E. I. Akeroyd and E. G. Stroud).

The Two Classes of Metals. Pilling and Bedworth[120] were the first to divide metals into two groups according as the oxide occupies a volume smaller or larger than that of the metal destroyed in producing it. If the density of an oxide be D and its molecular weight M, the volume (in ml.) occupied by one gram molecule will be M/D; if m is the weight of metal in M of oxide, and d the density of the metal, then the volume of metal destroyed in producing M of oxide will be m/d. Clearly, if $M/D < m/d$, that is, if $Md/mD < 1$, the oxide is likely to contain voids and may fail to isolate effectually the metal from the air. Calculation indicates that for the very light metals $\mathrm{M}d/m\mathrm{D}$ is less than unity; thus the values are Na 0·57, K 0·41, Mg 0·79, Ca 0·64. For the heavier metals, and two fairly light metals (aluminium and beryllium) it exceeds unity, the values being Be 1·70, Al 1·24, Fe 2·16, Ni 1·60, Cu 1·71, Zn 1·58. Observation shows that the very light metals of the first class really do produce porous oxides of no protective value, so that these metals, if heated in air, take fire and burn, giving out so much heat as to maintain their own temperature when the external heating is removed. The second class yield compact scales which clearly tend to shield the metal from the air; these metals do not burn in the massive state, although very thin wires (where the ratio of surface to volume is high) can be made to burn if strongly heated; the ignition temperature, as shown by Tammann and Boehme,[137] becomes lower as the diameter becomes smaller.

It was once believed that all metals of the first (light) class oxidize at a uniform rate (at constant temperature), owing to the non-protective character of the film, and that all those of the second (heavy) class suffer oxidation at a rate that falls off as the film thickens. Pilling and Bedworth's rectilinear curves for calcium (a light metal) and parabolic curves for copper (a heavy metal),[120] reproduced in Fig. 13, seemed to support this view. However, recent researches by Gulbransen [69] suggest that magnesium (a light metal) only gives rectilinear curves at temperatures sufficiently high to render the magnesium appreciably volatile. Conversely, early work by Vernon [147] makes it clear that zinc (a heavy metal), exposed at ordinary temperatures to polluted air, gives curves which remain straight for periods of many weeks (Fig. 16, p. 17).

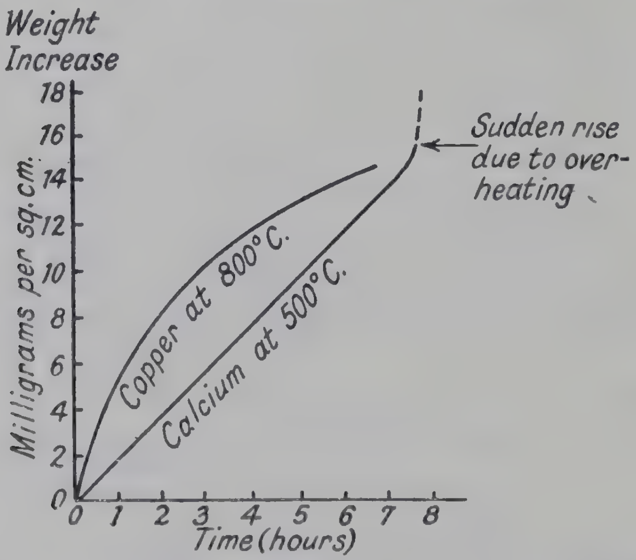

FIG. 13.—Growth of Oxide on Calcium and Copper (N. B. Pilling and R. E. Bedworth).

It should be noted that some metals can be heated in air without developing oxide films. This may occur when the oxide is volatile; molybdenum on heating in the open remains bright because the oxide formed passes off as vapour, although when heated in a closed tube the metal develops interference tints. On noble metals, oxidation may be absent altogether, if the temperature exceeds that at which the oxide would decompose. Silver, very gently heated, becomes slowly oxidized; but if the temperature is raised above 180° C., the decomposition pressure exceeds that of the atmosphere, and the oxide decomposes. Palladium, platinum and mercury develop visible films when moderately heated; at still higher temperatures the oxide decomposes. The case of mercury is historically interesting in connection with the discovery of oxygen.

Film Growth in the Brittle Range. Where the rate of oxidation falls off with time, the phenomena may vary according to the temperature, since the film substance will usually be plastic at high temperatures, but brittle at low ones. In the latter case the film may crack when it exceeds a certain thickness, so that the rate of film growth, previously slow, may suddenly become fast again. This is illustrated by comparing the curves of Pilling and Bedworth [120] for the oxidation of copper at 800° C. (Fig. 13, p. 12) with those at 500° C. (Fig. 14). At 800° a continuous curve is obtained, whereas at 500° oxidation, after it has begun to slow down, suddenly starts up again, owing to cracking. Another instructive example is provided by Vernon's measurements [147] on two specimens of aluminium exposed at ordinary temperatures to the atmosphere (Fig. 15). Here the film substance is highly protective, and corrosion is brought almost to a standstill whilst the film is still thin. However, seeing that alumina, if unconstrained, would occupy a much larger volume than the aluminium destroyed in producing it, it is clear that the film may remain in a state of lateral stress, and is thus liable to collapse. The curves suggest that (about the same time) the films gave way on both specimens, and rapid oxidation recommenced; presumably the damage to the original film,

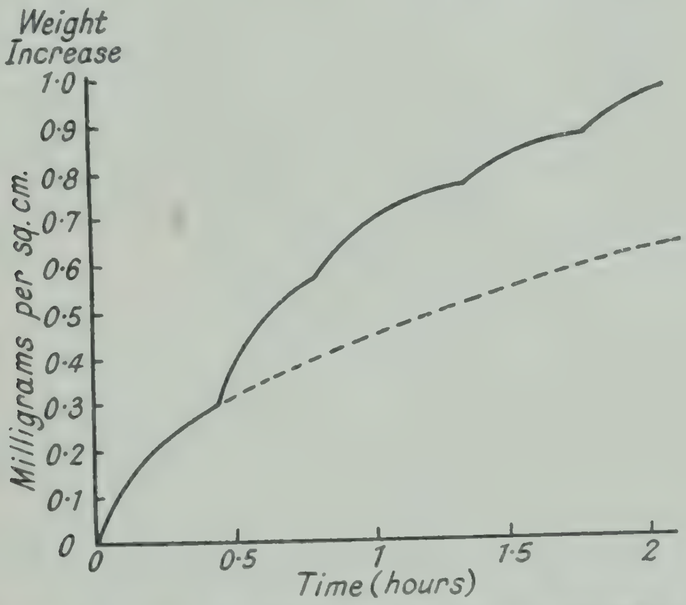

FIG. 14.—Oxidation of Copper at 500° C., measured by following the Increase of Electrical Resistance; data expressed as Weight-Increment (N. B. Pilling and R. E. Bedworth).

starting at one point, spread over the whole surface, so that a new alumina film had to be formed below the first; the same thing seems to have happened on subsequent occasions.

The idea of lateral stresses pent up in the films is not merely a matter of theory. These stresses really do exist, for when films are stripped by anodic undermining of the metal on which they rest,[54a] they develop wrinkles at the moment when they become loose, indicating that their natural area is greater than that which they are compelled to assume whilst attached to the metal. Film stress arises in more than one way.

Parabolic Law. At high temperatures complications due to cracking are absent. Oxidation usually depends on material passing through the crystal lattice. This is favoured by " vacant sites " in the crystal structure, such as are believed to occur in the oxides of metals of variable valency. The oxide of aluminium—a metal of fixed valency—is believed to have a composition accurately represented by Al_2O_3, but the composition of the oxides of iron and copper depart from the formulæ usually assigned to them. When the oxide is produced as a film on a metal, the composition will vary in depth. Iron heated above 575° C. becomes covered with three layers corresponding roughly to the three oxides FeO, Fe_3O_4 and Fe_2O_3, although the analyses of Pfeil[119] suggest that the lowest layer, which should be ferrous oxide, must at all parts contain less iron than the formula FeO would represent. The iron content also varies within each layer, being greater at the inner than at the outer surface of the layer.

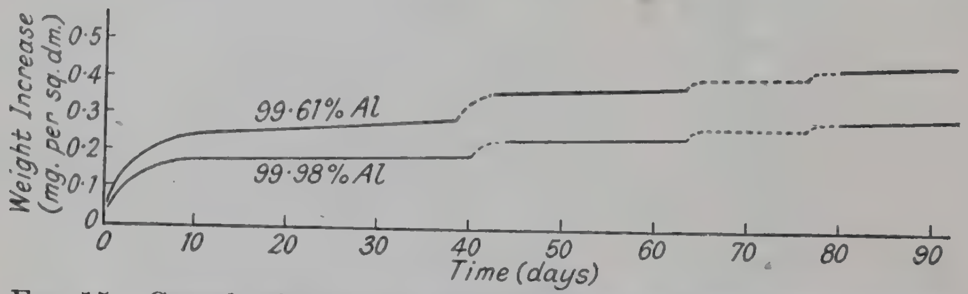

FIG. 15.—Growth of Oxide on Aluminium at Ordinary Temperatures (W. J. Vernon).

The so-called cuprous oxide usually contains less copper than the formula Cu_2O would suggest. A crystal of " perfect " cuprous oxide should consist of a lattice of oxygen anions interpenetrating a cation lattice consisting of twice the number of cuprous ions. In " imperfect " cuprous oxide, a certain number of points on the cation lattice are believed to be vacant, neutrality being preserved by the fact that at an equal number of points cupric ions exist where there would be cuprous ions in the perfect crystal. If this picture is correct, then clearly a mechanism is provided for the passage of metal outwards through the film; wherever there is a vacant space, a neighbouring cuprous ion can move into it, leaving another vacant space into which another cuprous ion can move, and so on. This movement, by itself, would involve an accumulation of electric charge, unless there is also a flow of electrons, which can come about in the following way. An oxygen atom attaching itself to the outer surface of a cuprous oxide film will absorb electrons from two cuprous ions, becoming an oxygen ion; the two cuprous ions will temporarily become cupric ions, but they can then absorb electrons from the cuprous ions farther in, and so on. Thus a regular passage of electrons, and of copper, occurs *outwards* through the film, and (provided that the supply of oxygen to the outer surface is maintained) the cuprous oxide layer steadily grows in thickness, the new oxide continually being deposited at the *outer* surface. Much definite evidence that oxidation depends on the *outward* movement of *metal*, rather than the *inward* passage of *oxygen*, has been obtained by Pfeil.[119] He showed, for instance, that if a "distemper" of chromic oxide powder is applied to iron before it is heated in air, the particles of chromic oxide become embedded in the oxide film, which has grown outwards and surrounded the particles.

The mechanism of oxidation just suggested demands that the film substance shall be *both* an *ionic* and an *electronic* conductor. The resistance to the movement both of ions and electrons must be proportional to the film thickness, and thus the rate of thickening of the film should be inversely proportional to the thickness, as represented by the equation

$$dy/dt = k/y$$

or

$$y^2 = \mathrm{K}t + \mathrm{K}'$$

which has already been mentioned as governing the growth of iodide films; but there the mechanism may be different. This parabolic equation has been established for the oxidation of copper about 800° C. by Pilling and Bedworth [120], and by Dunn [32] at lower temperatures. It is also obeyed by nickel, cobalt and tungsten; the values of the velocity constant (expressed in terms of weight increase per unit area) are quoted in Table VII.

If parabolic film growth consists of the outward movement of ions and electrons, it should be possible to express K in terms of the electrical properties of the film substance. An expression representing the dependence of K on the electrical conductivity was obtained by Wagner [160] and a simple proof, due to Hoar and Price,[83] is given on p. 191. The expression is

$$\frac{\mathrm{K}}{2} = k = \frac{\mathrm{J}n_e(n_c + n_a)\kappa\mathrm{E}}{\mathrm{DF}}$$

where F is Faraday's number, J the equivalent weight of the oxide (or other film substance), D its density, κ its specific conductivity, E the E.M.F. of the cell Metal | Metallic Oxide | Oxygen (or more generally Metal | Metallic Compound | Non-Metal) and n_e, n_c and n_a the three transport numbers for electrons, cations and anions in the film substance. In cases where the conductivity varies with the pressure of oxygen (or other non-metal involved), a more complicated equation (p. 192) comes into force.

TABLE VII

OXIDATION VELOCITY CONSTANTS w^2/t

(where w is the weight increase in grams per sq. cm. and t the time in hours) (J. S. Dunn and F. J. Wilkins)

Temperature	700° C.	800° C.	900° C.	1000° C.
Copper in O_2 .	$5{\cdot}86 \times 10^{-6}$	$3{\cdot}14 \times 10^{-5}$	$1{\cdot}27 \times 10^{-4}$	$6{\cdot}02 \times 10^{-4}$
,, ,, air .	$2{\cdot}68 \times 10^{-6}$	$2{\cdot}70 \times 10^{-5}$	$1{\cdot}10 \times 10^{-4}$	$4{\cdot}60 \times 10^{-4}$
Nickel (electrolytic) in O_2 .	—	$0{\cdot}093 \times 10^{-6}$	$0{\cdot}76 \times 10^{-6}$	$3{\cdot}4 \times 10^{-6}$
Nickel, grade A, in O_2 . . .	—	—	$1{\cdot}9 \times 10^{-6}$	$6{\cdot}8 \times 10^{-6}$
Cobalt in air .	$5{\cdot}8 \times 10^{-7}$	$3{\cdot}3 \times 10^{-6}$	$2{\cdot}2 \times 10^{-5}$	$7{\cdot}4 \times 10^{-5}$
Tungsten in air	$1{\cdot}61 \times 10^{-5}$	$16{\cdot}6 \times 10^{-5}$	$17{\cdot}9 \times 10^{-5}$	—
Tungsten in air (second sample)	—		$13{\cdot}4 \times 10^{-5}$	461×10^{-5}
Brass (95% Zinc) in air .	—	$2{\cdot}8 \times 10^{-5}$	—	—
,, (90% Zinc) in air .	—	$1{\cdot}69 \times 10^{-5}$	—	—

By means of this relationship the value of the oxidation constant has been calculated in three cases of film growth where the electrical values are known. In Table XIX (p. 193) the calculated values of the velocity constant (expressed in a slightly different form) are compared with the experimental determinations. The agreement is satisfactory, especially as the velocity constants are of different orders of magnitude in the different cases.

Rectilinear Law. Under conditions where cracking can occur in the film, the parabolic law will frequently cease to hold. If the cracks occur at infrequent intervals, a discontinuous curve must be expected (Fig. 14, p. 13). When there is a succession of little cracks following fast on one another, a practically smooth curve should be obtained. If fresh cracking only occurs when the passage of oxygen through the old cracks has produced a certain definite amount of new, compact oxide, then the overall rate of oxidation should remain roughly constant, just as a staircase consisting of many steps of identical size can be regarded, when viewed from afar, as a uniform slope. We should obtain, therefore, a straight line connecting thickness and time which can be written

$$dy/dt = k \text{ or } y = Kt$$

Any type of film which is cracked or porous, except at the lowest level where it adheres to the metallic base, is likely to develop according to this simple equation. Good examples of rectilinear growth are provided by Vernon's study of zinc exposed indoors in London (Fig. 16). Calcium, a light metal forming a porous oxide, also gives a straight-line oxidation-curve (Fig. 13, p. 12).

Logarithmic Law. Although cracks which run roughly at right ngles to the surface generally favour film growth, by facilitating either he inward passage of oxygen or the outward passage of cations, the pposite may be true of cavities lying parallel to the surface. If the ompressional stress causes the film to rise as a series of little blisters, ith a cavity under each, two cases must be considered. If the walls f the blisters are sufficiently cracked to admit oxygen to the cavity, resh oxidation of the metal at its base may occur, leading to rectilinear lm growth; in the case of Vernon's zinc specimens exposed to the olluted atmosphere of London, the presence of basic zinc sulphate may erhaps have weakened the film substance and rendered it "leaky". f the walls of the blister are practically airtight, as seems to be the case hen zinc is exposed to relatively pure air, the only mechanism of film rowth is the continued movement of zinc ions outwards. On the portion f the surface covered by a blister, the cavity will act as a barrier to the utward movement of cations, making film growth almost impossible. Thus continued oxidation must depend on outward movement from that art of the surface over which no such cavities have been formed. As he film thickens, the proportion of the total area which remains free rom cavity barriers diminishes, so that the rate of oxidation becomes ncreasingly slow. In such a case, the rate of oxidation should fall off ccording to the logarithmic equation

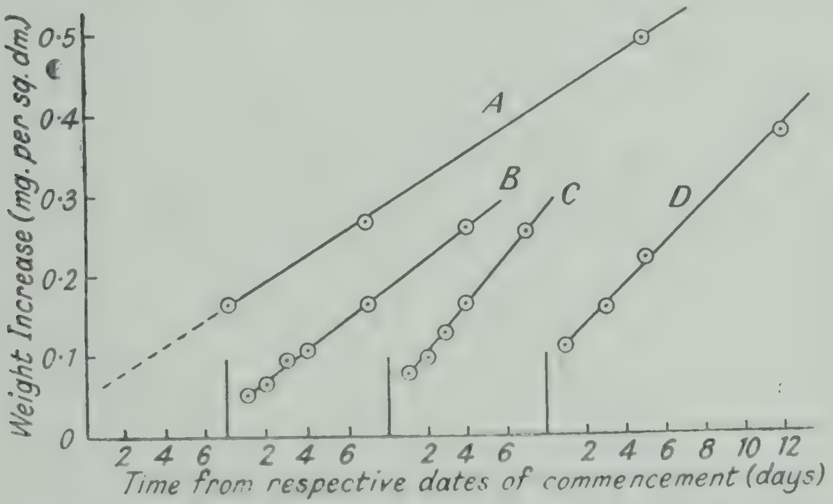

FIG. 16.—Atmospheric Corrosion of Zinc. Specimens started respectively on (A) Jan. 29, (B) April 24, (C) May 12, and (D) Aug. 19, 1925 (W. H. J. Vernon).

$$dy/dt = ke^{-k'y} \text{ or } y = \mathrm{K}\log(\mathrm{K}'t + \mathrm{K}'')$$

he derivation of which is given on p. 196. The extensive work of Vernon, Akeroyd and Stroud [153] on the oxidation of zinc exposed to pure air has stablished obedience to this logarithmic law over a wide range of emperature.

Dighton and Miley [28] state that around 250° C. copper first obeys the arabolic law and then the logarithmic law. Vernon found that iron beys the parabolic law at and above 200° C. but the logarithmic law between 50 and 195° C. On the whole, high temperatures favour parabolic and low temperatures logarithmic growth—as would be expected, since in oxides conductivity rises with temperature, whilst brittleness diminishes.

Relations between Electrical Properties and Protective Properties. Speaking generally, good resistance to oxidation may be expected if the electrical resistance of the oxide is high. The oxide of aluminium (and that of most metals of fixed valency) has a high electrical resistance, and it is noticeable that the oxidation of aluminium (Fig. 15, p. 14) practically ceases when the thickness has reached a certain low value and seems only to start again owing to the cracking of the film. The limited amount of oxidation which takes place between each breakdown does not obey the parabolic law. The fact that even this small amount of oxidation can occur has been attributed by Mott [114] to the fact that at thicknesses up to about 100 Å, electrons can reach the far side of a film, without activation energy, owing to the quantum-mechanical tunnel effect.

But there are exceptions to the rule associating oxidation-resistance with electrical resistance. Zinc oxide has a far lower electrical resistance than alumina, and yet its films exert considerable protection against oxidation. This is not only shown by the measurements of Vernon on zinc itself (p. 11), but by the studies of brass by Dunn,[32] who found that, at 600–900° C., those brasses which built up a film of pure zinc oxide were oxidized much more slowly than those which produced a film containing copper.

The discrepancy may be explained by the fact that passage through a film requires cationic conductivity as well as electronic conductivity. Now zinc oxide presents a marked contrast to cuprous oxide ; it contains *more* zinc than that suggested by ZnO, whereas cuprous oxide contains *less* copper than would be indicated by Cu_2O ; the contrast is shown by the fact that the conductivity of cuprous oxide increases, and that of zinc oxide diminishes, with increasing oxygen pressure (which will shift the compositions farther from Cu_2O and nearer to ZnO). If the vacant spaces in the cation lattice which permit of outward passage through cuprous oxide are absent from the zinc oxide lattice, there is no reason why zinc oxide should not be protective, despite the relatively high value of the electrical conductivity, as ordinarily measured, which is believed to be largely due to the movement of electrons.

It would seem, therefore, that two separate classes of oxide can provide protection,

(1) those like alumina, where the conductivity (κ) is low,

(2) those like zinc oxide, where ionic transport ($n_c + n_a$) is low.

It is believed that the highly protective films containing chromium belong to the second class.

Factors Influencing Service Life

Alloying of Iron and Copper to obtain Protection. It might be thought that since, at high temperatures, the oxidation rate becomes increasingly slow as the oxide scale thickens, ordinary steel would become lmost immune to oxidation when the scale had become sufficiently thick. n engineering practice, however, thick scale would break off when the art was rubbed or bent, or when the temperature was allowed to cool own; cooling produces stresses due to the unequal contraction of metal nd oxide, and also renders the scale brittle, so that these stresses cannot e relieved by flow. At very high temperatures special steels are used ontaining alloying elements which make the scale protective when it is till very thin; thin films are unlikely to become detached, because the nternal compressional energy per unit area available for detachment is nuch smaller than in thick films, whereas there is no diminution of the vork needed to detach unit area.

Even on alloys which develop films possessing protective properties t very small thicknesses, the oxidation rate is much greater under conlitions of fluctuating temperature than at constant temperature. The iickel-chromium wires used in electric heaters and furnace-elements uffer far more oxidation if heated intermittently than continuously; he oxide film formed at high temperatures tends to crack off on cooling. In industry these wires are subjected to tests designed to gauge their ower of resisting detachment on alternate heating and cooling, and ometimes on alternate coiling and straightening.

The elements commonly added to steel used in making furnace parts, ngine components or heat-treatment boxes, in order to confer resistance gainst oxidation at high temperatures, are *chromium* and *aluminium*. Along with chromium, nickel is often introduced to give a one-phase, ustenitic structure, and, since the straight austenitic steels, such as the vell-known 18/8 chromium-nickel stainless steel (p. 86), would be too veak at high temperatures for practical use, small quantities of other lements, such as silicon and tungsten, are added to improve the mechanical properties. Straight iron-aluminium alloys, although highly resistant to oxidation (provided the aluminium content is sufficient to give a white scale of alumina instead of the dark scale characteristic of nalloyed iron), are mechanically unsatisfactory. In practice, iron and steel furnace parts, annealing boxes and the like are often given a superficial layer of iron-aluminium alloy by heating them in a mixture of powdered aluminium, alumina and a little ammonium chloride; after this treatment, the oxidation-resistance is wonderfully improved, without serious deterioration of mechanical properties.

Special cast irons intended for parts which have to be heated and cooled alternately often contain nickel and chromium, in amounts chosen to stabilize the austenitic state. This avoids the susceptibility to the so-called "growth" (volume-increase) displayed by ordinary grey cast iron after being heated and cooled many times through the $\alpha \rightleftharpoons \gamma$ change-point. Growth is essentially an oxidation process, but the penetration of oxygen (especially along coarse graphite flakes) is facilitated by the volume-changes associated with the $\alpha \rightleftharpoons \gamma$ transformation.

Of the protective elements mentioned above, the resistance conferred by aluminium is due to the formation of films of low *electronic* conductivity, whereas that due to chromium is considered by Hoar to be due to films of low *ionic* conductivity. This has not been proved, but, by analogy with ferric oxide (which contains more iron than the formula Fe_2O_3 would indicate), Cr_2O_3 is likely to be free from vacant places in the cation lattice, and hence might be expected to be protective. It may well be asked why Fe_2O_3 is not protective also. But here it must be remembered that at high temperatures the ferric oxide film is the *outermost* layer of a triple film (p. 143) and in such a situation it is likely to crack under the forces present. Chromic oxide and alumina are stronger substances; on heating steels containing chromium or aluminium, these oxides are found at the *base* of the film, in close contact with the metal, as shown by Portevin, Prétet and Jolivet.[121] Neither aluminium (an element only found in the trivalent condition) nor chromium (the divalent compounds of which are unstable) is likely readily to enter the ferrous oxide layer. They accumulate, therefore, in the steel, until they separate out as sesquioxides, forming a layer of real protective character.

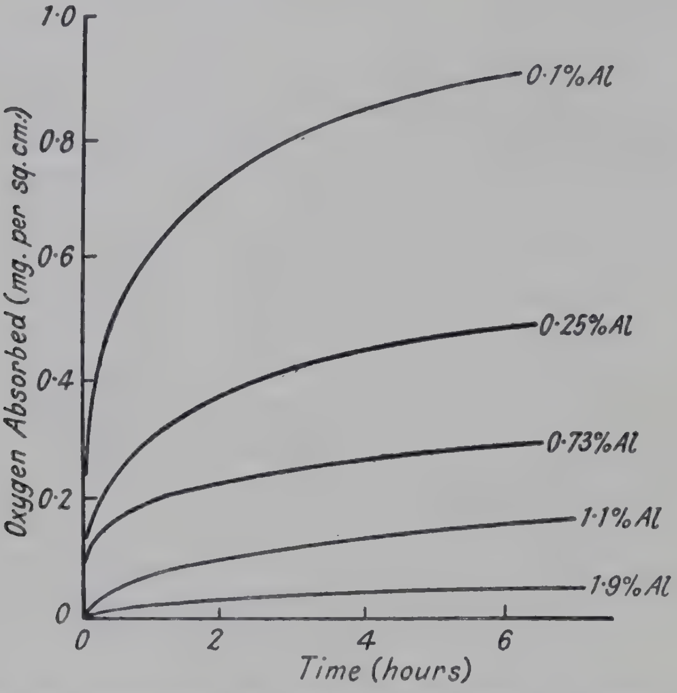

Fig. 17.—Effect of Aluminium on Oxidation of Brass at 775° C. (J. S. Dunn).

Aluminium greatly improves the resistance of copper and brass to oxidation at high temperatures and also to low-temperature corrosion by atmospheres polluted with sulphur compounds. The effect on brass is shown by Dunn's curves,[32] reproduced in Fig. 17. The influence of different alloying elements in copper was studied by Fröhlich.[62] Price and Thomas,[123] surveying his results, pointed out that the only elements which greatly improve the resistance to oxidation are those like aluminium and beryllium, whose oxides possess high electrical resistance. Among metals possessing oxides of high conductivity, only zinc brings benefit; this apparent exception has been discussed on p. 18.

Qualitatively, Fröhlich's results seem to fulfil the predictions of heory; quantitatively there appeared, at first, to be discrepancies. Price and Thomas calculated that, if the resistance conferred by aluminium was due to an alumina film, the resistance should be raised at least 80,000 imes; actually it was increased only 36 times. They suggested that this disappointing result might be due to the presence of copper oxide n the alumina film, which would lower the electrical resistance and hence the protective properties, and predicted that, if a film of copper-free alumina could be obtained on the alloy, the resistance to oxidation would be enhanced. Accordingly they heated the alloy in hydrogen containing a trace of water vapour (0·1 mm. of mercury), which was expected to oxidize aluminium (an element with high affinity for oxygen) but not copper. This treatment produced no visible change in the alloy, but evidently an invisible protective film was really formed, since when subsequently the alloy was heated in oxygen under conditions which produced a dense black layer on the untreated alloy, the appearance remained unaltered. Quantitative experiments indicated that the resistance had improved about 200,000 times—the order of magnitude predicted by theory.

This success provided confirmation of the theoretical views which had led up to the protective treatment, whilst the treatment itself, now known as *Selective Oxidation*, is likely to have practical value in securing improved resistance to oxidation and tarnishing in the years to come.

Oxidation by Products of Combustion. The gases formed when coke is burnt in air consists mainly of nitrogen, carbon dioxide and a little water vapour; with coal or oil as the fuel, the products of combustion contain more water and less carbon dioxide, whilst there is still more water present in the mixture obtained on burning coal gas. If air has been admitted to a furnace in excess, oxygen will also be present, and this will enhance the oxidizing powers of the mixture; but even if free oxygen is absent, oxidation is still possible, as shown by the extensive studies of Cobb and his colleagues.[22] Carbon dioxide can oxidize steel, unless the ratio $CO:CO_2$ in the mixture exceeds a certain value which depends on the temperature. Equally dangerous is water vapour, and its presence in the combustion products of coal gas makes them very destructive, even if oxygen is absent. If the mixture is cooled so as to deposit most of its moisture, and if unburnt gas is then added, most of the scale-producing power disappears; if water is not eliminated, the amount of unburnt gas needed to render the mixture harmless is excessive. In all these gas mixtures, the presence of compounds of sulphur greatly increases the destructive power, as shown below.

In annealing non-ferrous metal parts, it is desirable to use an atmosphere which will cause neither oxidation nor tarnishing. The exclusion of sulphur compounds is particularly important, and if coal gas is used in the "bright annealing" of nickel, copper or their alloys, it should be partially burnt, purified by passing through bog iron ore and peat and cooled to precipitate water vapour; a suitable analysis for the gas entering the furnace is 6% CO_2, 9% CO, 11% H_2, 1·5% H_2O (rest nitroge Butane, which contains no sulphur, is useful in bright annealing, ammonia " cracked " (decomposed) in presence of a catalyst may be use Another method is to lead a mixture of carbon monoxide and dioxide ov charcoal heated electrically at a temperature controlled to give the desir $CO:CO_2$ ratio. For copper, atmospheres very rich in hydrogen shou be avoided, as hydrogen acts on intergranular oxide, producing stea internally, which may lead to brittleness.

For the heat-treatment of steel, the atmosphere—besides being no oxidizing—should be " neutral " in the sense that it will neither increa nor reduce the carbon-content.* If coal gas is used, it may be passe through heated tubes before entering the furnaces, so as to decompose t hydrocarbons ; by regulating the rate of flow, the desired ratio of metha to hydrogen can be obtained ; the ratio required increases with t carbon-content of the steel. Burnt ammonia (i.e. ammonia burnt with controlled quantity of air, so as to give a mixture of nitrogen wit 5–15% hydrogen) has found employment for treating steel.

Sulphur Compounds. The metal-deficit of a sulphide often excee that of an oxide, pointing to a larger number of holes in the lattice an diminished protective power. The mineral *pyrrhotite* is assigned t formula $Fe_{11}S_{12}$ in some old mineralogy books ; it is now regarded FeS with 1/12 of the cation sites vacant. Cuprous sulphide also contai less copper than the formula Cu_2S would indicate. It is not surprisin to find that copper, exposed to air containing hydrogen sulphide, rapidl develops visible films at ordinary temperatures ; the sequence of colou is the same as that produced in pure air at slightly elevated temperature but the films, containing copper sulphide, are much less protective, s that the interference colour range is reached and passed at ordinar temperatures.

The behaviour of iron in furnace gas varies greatly with the sulphu content, and wastage may be reduced by using fuel low in sulphur ; coa for instance, can have its sulphur-bearing minerals largely removed b washing. The presence of sulphur modifies the law governing oxidatio A relatively protective film would follow the parabolic law, so that th weight of oxide (W) formed in time t would be given by $W^2 = Kt$; completely unprotective scale would permit of an oxidation rate whic did not diminish with time, $W = Kt$. For practical purposes, Taylo and Cobb [139] write $W^n = Kt$, where n varies between 1 and 2, diminishin with increase of sulphur compounds and with rise in temperature.

The presence of sulphur in the furnace gas may also cause the oxidatio to penetrate down into the steel along the intergranular boundaries— apart from the formation of a scale ; this is particularly important i steels containing nickel and copper.

Sulphur compounds may, however, affect oxidation in another way The oxidation rate always suddenly increases when the scale melts ; th pure oxide scale formed in the absence of sulphur melts about 1340° C, nd above this temperature the oxidation becomes very rapid—being nainly determined by the rate at which gases containing oxygen are lown over the surface. If sulphur is present, a sulphide-oxide eutectic nay be formed melting below 1000° C., so that in the range 1000–1340° C. ılphur will greatly accelerate the attack. If nickel is present in the netallic phase, a molten eutectic may appear as low as 625° C.; certain lloys rich in nickel are attacked much faster in presence of sulphur ompounds than in their absence.

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* It should also be one which does not introduce hydrogen.

Tarnishing. Whilst copper exposed indoors to town air below the ritical humidity (p. 80) develops interference tints, its exposure indoors ɔ the same air at high humidities generally produces an unattractive ale brown tint, due to a film containing both oxide and sulphide. If he ordinary air is filtered through silver powder, which removes the ulphur compounds, it loses its tarnishing power, as shown by Vernon.[147] Ie also demonstrated that a long exposure of copper to pure air greatly educes its susceptibility to tarnishing when subsequently exposed to air ontaining sulphur compounds, since an invisible oxide film is formed in the rst stage which is far more protective than the film containing sulphide.

Silver also develops an ugly tarnish-colour when exposed to an atmophere containing sulphur compounds. The reactions are complicated; rice and Thomas,[124] studying the tarnish film produced on Sterling ilver (with 7·5% copper), detected four compounds, silver sulphide, uprous sulphide, cuprous oxide and silver sulphate; the electrometric nethod is capable of identifying all these compounds, since they suffer eduction at different potentials.

Price and Thomas also showed [123] that if, instead of ordinary Sterling ilver, an alloy with 6·5% copper and 1% aluminium (which complies ith the legal definition of Sterling Silver) is adopted, and subjected to elective Oxidation by heating in hydrogen with a trace of water vapour see p. 21), so as to develop an invisible film of alumina free from silver, ıe surface becomes remarkably proof against tarnishing, although in ıe untreated state this alloy is hardly more resistant to tarnishing than ure silver.

Pure or Sterling Silver (containing no aluminium) was rendered esistant to tarnishing by depositing on it a film of beryllia by cathodic reatment in a solution of beryllium sulphate containing enough ammonia ɔ bring the composition between $BeSO_4.Be(OH)_2$ and $Be(OH)_2$. Such solution contains positively charged colloid particles, which probably nigrate to the cathode. (An alternative explanation is that alkali proluced by the cathodic reaction precipitates the beryllia.) If the conitions are adjusted properly, the film is invisible, but its existence can e demonstrated by placing a sheet of thin film-covered silver on mercury, hich dissolves the silver and leaves the film floating.

Direct Attack on Metals by Dissolved Oxygen

General. Parson's principle (p. 1) would suggest that oxygen issolved in water should have little action on the majority of metals, since, with the exception of the alkali and alkaline earth metals, and also thallium, the solubility of the oxides and hydroxides is very low Experimental observations confirm that the corrosion of metals by distilled water containing oxygen is actually slight, although, as shown below it is often by no means negligible.

Lead. Pure water containing oxygen produces on lead not a continuous protective film, but an open network of beautiful crystals Apparently the “nucleus number” of lead oxide is low, so that the actual number of crystals formed per unit area is limited. This open network is naturally less protective than a continuous film consisting o a very large number of extremely small crystals, and the corrosion o lead by distilled water cannot be neglected.

Zinc. The protective film formed by distilled water acting on zinc is probably hydroxide, and extends over nearly the whole surface. At certain points, however, the metal remains uncovered, and the passage of zinc into solution at these points keeps undermining and breaking of the film, so that local attack continues. Although the total quantity o metal destroyed is not large, the corrosion is concentrated on these few points, where the pitting may be quite serious. The quantitative experiments of Bengough, Stuart and Lee [8] on zinc in very pure water containing oxygen gave curves somewhat recalling Vernon's curves for the atmospheric attack on aluminium (Fig. 15, p. 14); the corrosion seem to come to rest, and then suddenly starts up again, probably indicating that the film has cracked and broken off.

Iron. The situation on iron is complicated by the two states o oxidation. Ferrous hydroxide ($Fe(OH)_2$) is much more soluble than ferric hydroxide (actually a partial hydroxide, $Fe_2O_3.H_2O$ or $FeO(OH)$)) If a disc of pure iron in distilled water containing oxygen is whirled so fast that oxygen is kept in excess at all points on the surface, it undergoes practically no visible change, presumably because a film of ferric hydroxide is produced so close to the surface as to smother attack whilst the film is still too thin to be visible. But the same iron placed in the same distilled water under stagnant conditions will develop rust. Ferrous hydroxide is formed at the metallic surface, and is converted to ferric hydroxide (yellow rust) at a little distance away, where there is more oxygen. This conversion renders the water unsaturated with respect to ferrous hydroxide, and thus prevents effective stifling by means of a ferrous hydroxide film; the ferric hydroxide—formed at a perceptible distance from the surface—is non-protective.

The matter has been studied statistically by Mears and the author.[11] Two sets of waxed lines at right angles were ruled on a clean iron plate which was flooded with water and then tilted so as to let the excess run off leaving a chess-board pattern of “square drops” covering the unwaxed squares. Experiments were carried out in vessels containing mixtures o oxygen and nitrogen. Owing to differences in the invisible oxide film present on the iron surface, the drops did not all behave alike. In general some developed rust and others did not. In mixtures rich in oxygen he proportion developing rust was smaller than in mixtures poor in xygen. On the other hand, in those drops where any rust was produced t all, the rate of corrosion was most rapid in the more oxygen-rich tmospheres. This is to be expected, since the nearer the position of the onversion of ferrous hydroxide to ferric hydroxide comes to the site of orrosion, the steeper will be the concentration gradient, the more rapid he diffusion of ferrous hydroxide from the points of attack, and consequently the faster the corrosion of the metal itself. It is only when the oxygen concentration is so high as to bring the position of conversion into physical contact with the metal that stifling sets in. Thus it comes about

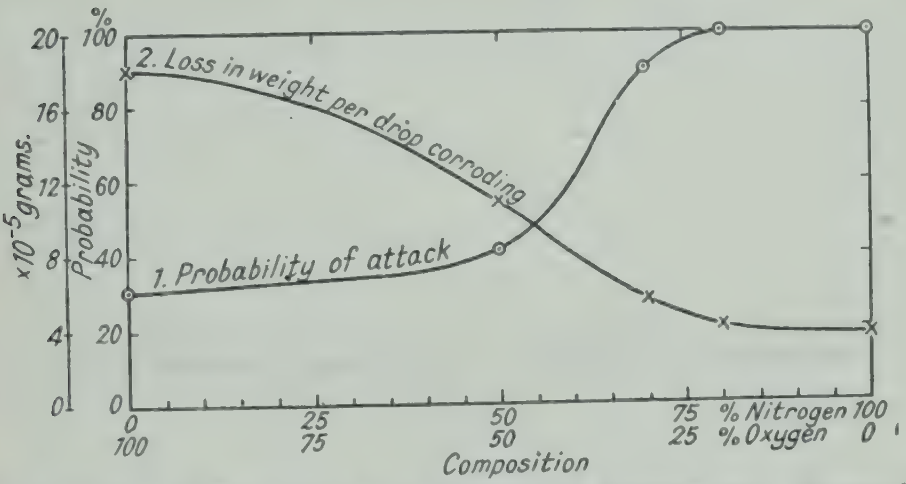

FIG. 18.—Variation of Probability and Conditional Velocity with Oxygen-Content (U. R. Evans and R. B. Mears).

that oxygen is a *stimulator* of corrosion in the sense that it increases the *conditional velocity* (the velocity produced on the condition that there is any corrosion at all), but a *deterrent* of corrosion * in the sense that it reduces the *probability* of attack starting. Mears's curves are shown in Fig. 18.

It is evident that direct attack on metals by oxygen dissolved in water is not impossible. Nevertheless, the total destruction caused in this way is usually small. As shown in the next chapter, *electrochemical action*, which frequently leads to soluble compounds as the primary corrosion products, is often far more destructive.

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* A *deterrent* is a chemical which reduces probability; an *inhibitor* is a chemical which decreases velocity. Many inhibitors are also deterrents.

The author's views on film growth are presented in greater detail in a paper delivered to the Electrochemical Society in April 1947, which will appear in Vol. 91 of the *Transactions* of that society. New experimental evidence of internal stress in films is provided in a paper to be delivered in October 1947 at the Symposium on Internal Stresses, organized by the Institute of Metals.

CHAPTER II

ELECTROCHEMICAL CORROSION

Electrochemical Action without Applied E.M.F.

Corrosion at a Break in Oxide Scale. Imagine a piece of ir which has been coated with a thick oxide scale by heating in air; suppo that the scale has cracked off over one small area, exposing the met and that the specimen is then immersed in sodium chloride soluti containing oxygen * (Fig. 19). An electric current will flow between t oxide scale as cathode and the bare metal as anode. The current w only remain strong if oxygen has access to the cathodic surface, where will react according to some such equation † as :—

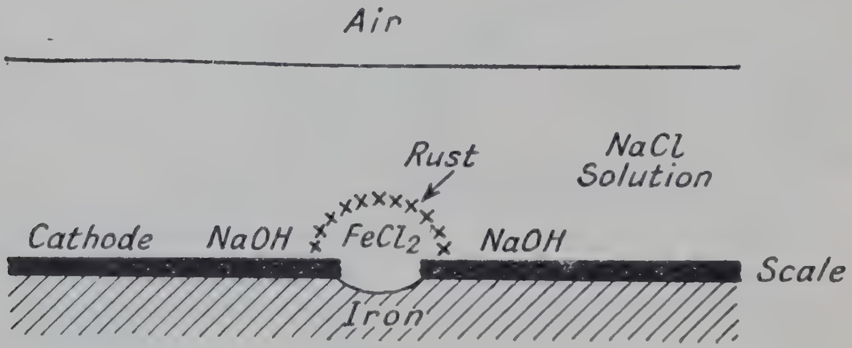

FIG. 19.—Corrosion at Breaks in Oxide Scale on Iron immersed in Sodium Chloride Solution.

$$O + H_2O + 2e = 2(OH)'$$

At the anodic area, the iron will pass into solution, usually as ferrous ion according to the equation

$$Fe = Fe^{\cdot\cdot} + 2e$$

Since sodium ions and chlorine ions are already present in the solutic we can regard the cathodic product as being sodium hydroxide and th anodic product as ferrous chloride. Both of these are freely soluble bodie and will not stifle attack. They will, however, yield solid substanc where they meet; ferrous hydroxide ($Fe(OH)_2$) may be momentaril precipitated, but if oxygen is present in sufficient quantity, it will b immediately oxidized to ferric hydroxide; this substance, commonl known as *yellow rust*, is $FeO(OH)$ or $Fe_2O_3.H_2O$, not $Fe(OH)_3$. If th supply of oxygen is limited, the product may be green hydrated magnetit or black anhydrous magnetite, Fe_3O_4.

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* The most pronounced pits are obtained if the solution is made slightly alkaline. A acid solution would behave differently; there would be no pitting, the film being reduce and dissolved, as explained on p. 42.

† Some authorities write this $\frac{1}{2}O_2 + H_2O + 2e = 2(OH)'$.

It will be noticed that this electrochemical corrosion ultimately brings about a combination of iron with oxygen (and usually with water) yieldng an oxide or hydroxide. It differs from direct oxidation, however, n that the iron goes into solution at *one* place, the oxygen is taken up at a *econd* place, and the oxide, or hydroxide, is formed at a *third* place; hus the solid corrosion product, formed at a distance from the point of attack, cannot stifle the action. It is on this account that electrochemical corrosion is often more dangerous than direct oxidation.

Another point deserves notice. The strength of the current flowing depends largely on the amount of oxygen reaching the cathode, and if he cathode, the scale-covered portion, is large, the current may be quite trong in relation to the size of the anodic area. The whole of the corrosive effect falls, however, on the anode, the bare portion of the metal. Thus the attack may become very intense when the exposed portion of he iron is small. *Intense attack* is very frequently associated with this combination of *large cathode and small anode.*

Pitting is often met with in chemical and engineering practice at small gaps in the mill-scale covering mild steel plate, pipes or sheets. Removal of mill-scale from pipes or containers has been found to diminish the rate at which local corrosion bores down into the metal.

Other Sources of Corrosion Currents. Clearly electric currents can be generated in other ways than by junction between oxide scale and metal. If the specimen in Fig. 19 had consisted of two different metals, such as copper and iron, a current would have been generated, the attack falling on the iron, the anode of the " couple ". Intense attack is sometimes met with on iron carrying a copper coat which has been broken locally, perhaps at a bend, so that a small anode of bare iron is surrounded by a large cathode of copper. In a salt solution, the attack may then be locally more intense than if no attempt had been made to provide a protective coating.

Corrosion currents may also be set up if one part of a piece of iron has been bent, since deformation will damage any invisible oxide film present, and is believed to render the metal itself less stable, by disturbing the crystal arrangement. But one of the most important ways in which corrosion currents arise is by differences of oxygen distribution in the liquid—as described below.

Whatever the origin of the current, the amount of corrosion can be obtained by means of Faraday's law (p. xxi) if the current strength be known; 96,487 coulombs will cause the anodic corrosion of one gram equivalent of any metal; thus 1 ampere-hour will corrode 1·22 grams of zinc, 1·04 grams of iron (as a ferrous compound) or 3·86 grams of lead.

Differential Aeration Currents. Early experiments by the author [34] showed that if two electrodes of iron joined by wires to a milli-ammeter are placed in the two compartments of a divided cell, and if oxygen (or air) is bubbled through one compartment (Fig. 20), a " differential aeration current " is registered, the aerated electrode being the cathode; when the current of oxygen is diverted to the other compartment, the direction of the current is reversed. If the experiment is repeated with zin electrodes, the same result is obtained, the currents being stronger. Wit cadmium electrodes, the effect is much weaker, often no greater than th small current set up between two cadmium electrodes in the absenc of bubbling (no two pieces of metal are exactly equi-potential); bu even in such cases a differential aeration effect can be observe since the passage of oxygen over that electrode which, in the absenc of bubbling, had been the cathode, increases the current, whilst th

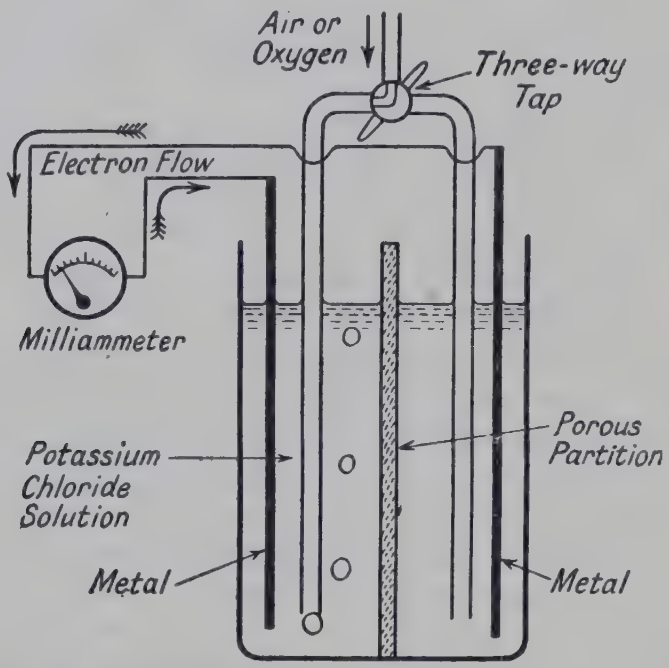

Fig. 20—Generation of Differential Aeration Currents between Electrodes of the sam Metal in the same Liquid, Oxygen being bubbled over one Electrode only (Schematic

aeration of the electrode which had been the anode diminishes or eve reverses the current.*

Corrosion by Drops. The author's experiments [35] suggested tha differential aeration currents are responsible for the distribution o corrosion produced by drops of sodium (or potassium) chloride (or sulphate solution placed on horizontal sheets of iron or zinc. A drop of sodiu chloride solution resting on iron sets up attack at the centre, wher ferrous chloride is formed, whilst the peripheral zone remains immun from attack, sodium hydroxide being there produced ; a ring of yello rust appears where the alkali and iron salt meet and interact. Thi distribution is connected with electric currents flowing between a centra anode and a cathode at the periphery, where oxygen, the cathodic reactant can best be replenished. In special experiments where the flanks of the drop were surrounded with nitrogen, and oxygen was blown down upon the centre, the author found the distribution to be reversed, the centre being immune and the periphery attacked. In other experiments where large drops of sodium bicarbonate were employed, it was found possible actually to detect the electric currents.

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* The case of copper appears anomalous, since the stirring set up by the bubbles remove the copper ions from the neighbourhood of the electrode over which bubbles are passing thus shifting the potential in the negative direction (see p. 96) ; this renders the electrod concerned anodic towards the other. On copper, the differential aeration effect, althoug capable of demonstration, is feeble, and is usually outweighed by the stirring effect, wherea on zinc or iron the differential aeration effect far surpasses the stirring effect.

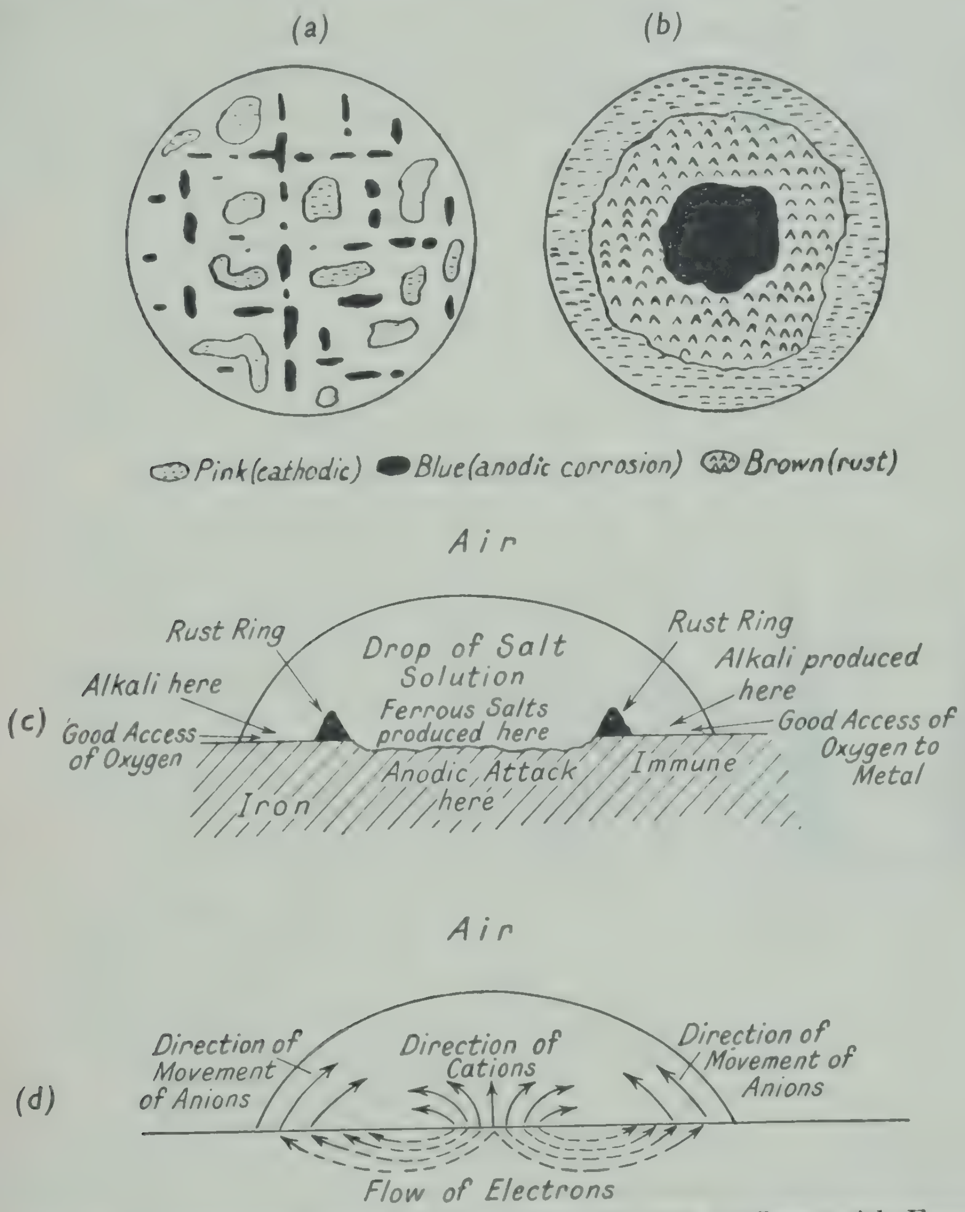
(a)
(b)
Pink(cathodic)
Blue(anodic corrosion)
Brown(rust)
Air
Rust Ring
Drop of Salt Solution
Rust Ring
Alkali produced here
Alkali here
Ferrous Salts produced here
(c)
Good Access of Oxygen
Good Access of Oxygen to Metal
Anodic Attack here
Immune
Iron
Air
Direction of Movement of Anions
Direction of Cations
Direction of Movement of Anions
(d)
Flow of Electrons

FIG. 21.—Action of Drops of Potassium Chloride on Iron, with Ferroxyl Indicator to show up Anodic and Cathodic Areas.

Experiments were also performed with drops of potassium chloride solution containing small amounts of *ferroxyl indicator* (phenolphthalein + potassium ferricyanide), which serves to show up the cathodic places (where alkali is produced) as pink patches and the anodic places (where iron salts appear) as blue points. If the solution contains oxygen at the outset, the primary distribution (Fig. 21 (*a*)) is an irregular pattern of blue and red. When the original oxygen has been used up, the red colour becomes confined to the peripheral zone, since only here can oxygen b readily replenished; at the same time, the blue points disappear fron the peripheral zone, since, when once alkali (the cathodic product) ha here been formed in excess, any iron salts formed momentarily will b precipitated in physical contact with the metal and will stifle furthe attack. Thus the secondary distribution (Fig. 21 (*b*)) will be a pinl ring separated from a blue centre by a brown circle of rust. The tim needed to pass from the primary to secondary distribution naturall depends on the original oxygen concentration; if the liquid is supersaturated with oxygen, the primary distribution remains abnormall long, whereas, if dissolved oxygen is removed before the drop is placec on the metal, the secondary distribution arrives at once. Fig. 21 (*c*) and (*d*) represent sections of the drop during the secondary stage, and show the chemical and electrical phenomena respectively.

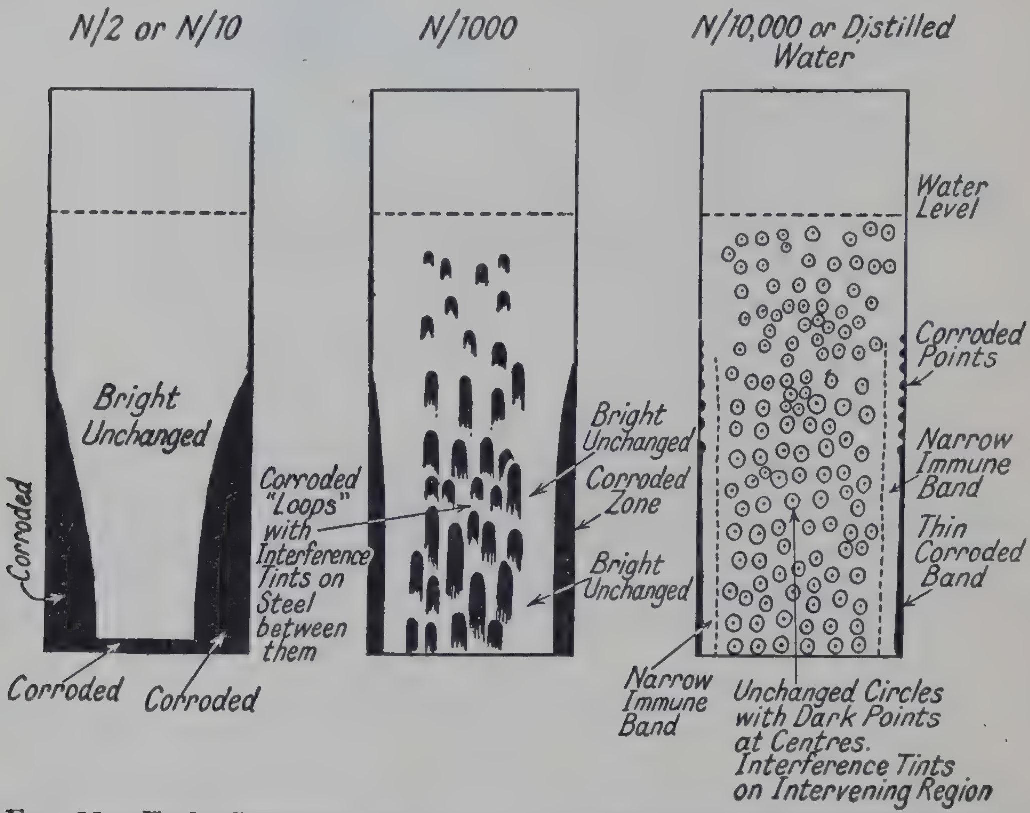
N/2 or N/10
N/1000
N/10,000 or Distilled Water
Bright Unchanged
Corroded
Corroded
Corroded
Corroded "Loops" with Interference Tints on Steel between them
Bright Unchanged
Corroded Zone
Bright Unchanged
Water Level
Corroded Points
Narrow Immune Band
Thin Corroded Band
Narrow Immune Band
Unchanged Circles with Dark Points at Centres. Interference Tints on Intervening Region

FIG. 22.—Early Stages of Attack on a Steel Plate by Sodium Chloride of Different Concentrations.

Corrosion of Vertical Iron Plates. Similar principles govern the distribution of corrosion on vertical iron plates partially immersed in a solution of sodium (or potassium) chloride (or sulphate).[34] During the first few days, the zone along the water-line, where oxygen can best be renewed, remains immune (being cathodic), whilst there is anodic corrosion a little lower down; along the line bounding the anodic region, there is a "mantle" of membranous rust. With uniform, specially prepared, steel, the corroded (anodic) zone may (in reasonably concenated solutions, say N/10) be confined to the neighbourhood of the cut dges, which, largely owing to interruption of the invisible oxide film, is nodic to the rest; this pattern is called the "Ideal Distribution" Fig. 22). The corroded zone usually moves upwards towards the waterne, sometimes discontinuously (Fig. 23), so that a number of mantles re formed in turn at increasingly high levels. On some specimens the orrosion may finally reach the water-line; the cathode is probably then he portion above the water-line which has become damp through the reepage of alkali upwards and is freely accessible to oxygen. In the Cambridge experiments, provided that care was taken to avoid thermal onvection currents (which would keep removing the protective alkali ormed at the water-line) and to exclude carbon dioxide (which would destroy the alkali), a protected zone has usually remained at the waterline for several weeks.

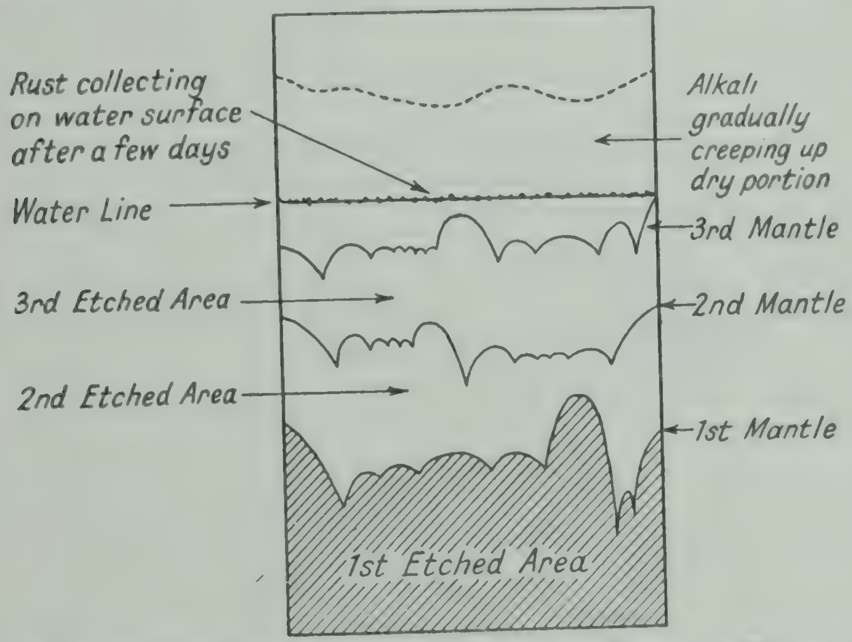
Rust collecting on water surface after a few days
Alkali gradually creeping up dry portion
Water Line
3rd Mantle
3rd Etched Area
2nd Mantle
2nd Etched Area
1st Mantle
1st Etched Area

FIG. 23.—Discontinuous Advance of Corrosion Upwards (Schematic).

At greater dilutions, the distribution is more irregular, and in the early stages attack tends to be most severe at certain "susceptible points" (often inclusions or surface defects), which (in the later stages of attack) form the tops of the "arches" in the sinuous mantle.

Corrosion of Vertical Zinc Plates. A rather similar distribution of attack is observed on zinc, although behaviour varies with surface condition. Corrosion starts at a larger number of points on a rough surface than on a smooth one, so that the mantle is more sinuous; it is less sinuous in sulphate than in chloride solution, and the white corrosion product (zinc hydroxide or basic salt) is precipitated closest to the metal when divalent $(SO_4)''$ ions are present, so that in sulphate solutions much white matter is found clinging to the zinc surface. As on iron, there is a tendency for the corroded portion to move upwards with time; sometimes on rolled zinc the upper boundary of the corroding area is perfectly horizontal (Fig. 24 (A)) and moves upwards continuously wi time (instead of intermittently with the formation of successive men

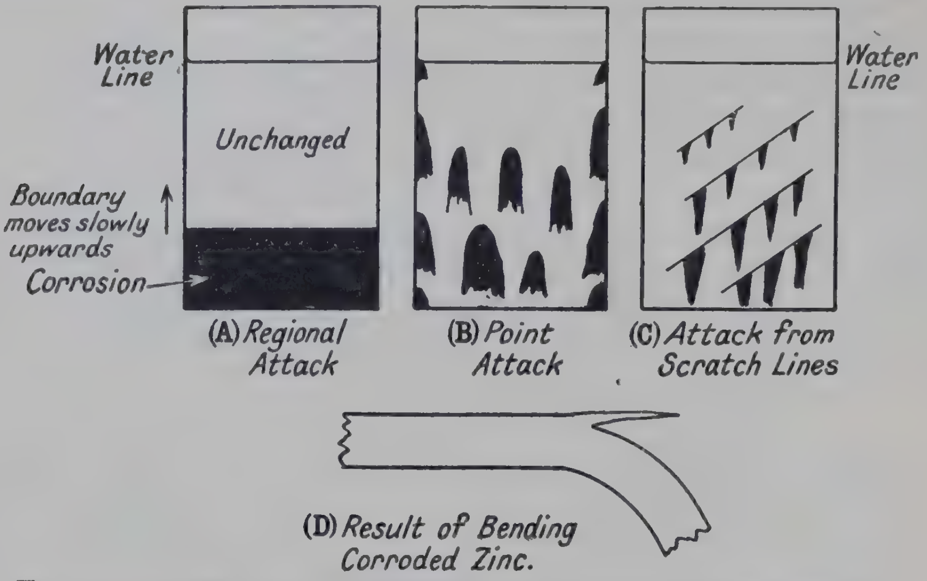
Water Line
Unchanged
Boundary moves slowly upwards
Corrosion
(A) Regional Attack
(B) Point Attack
(C) Attack from Scratch Lines
Water Line
(D) Result of Bending Corroded Zinc.

FIG. 24.—Distribution of Corrosion on Zinc with Rolled Surface.

branes). Often corrosion ultimately reaches the water-line, and is ther usually most intense at that level; in the experiments of Bengoug and Wormwell[8] perforation occurrec along the water-line at a stage wher there was no perforation anywhere else In some cases, attack starts from sus ceptible points or from scratch-lines, i present (Fig. 24 (B) and (C)). Often or rolled zinc attack penetrates parallel tc the surface along internal laminations, sc that on bending a specimen which has corroded for some weeks, the surface layers part company from the layers below them (Fig. 24 (D)).

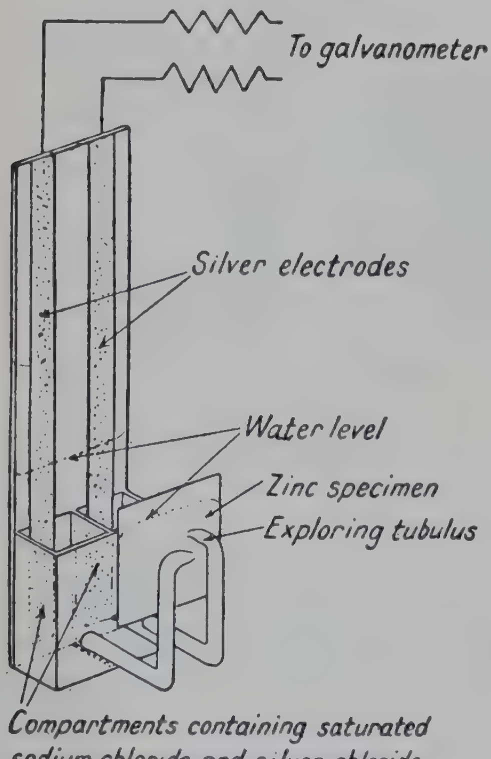
To galvanometer
Silver electrodes
Water level
Zinc specimen
Exploring tubulus
Compartments containing saturated sodium chloride and silver chloride

FIG. 25.—Dielectrode for detecting Anodic and Cathodic Points on Zinc in Sodium Chloride Solution.

The experiments of Thornhill[143] at Cambridge provide evidence of the electrochemical character of the corrosion on zinc. He used an apparatus called a "dielectrode" (Fig. 25) to distinguish anodes and cathodes. This consists of two Ag | AgCl electrodes provided with tubuli protruding to different distances and joined to a micro-ammeter with central zero-point; one tubulus is pushed into contact with the zinc surface at the point where the polarity is to be tested. If current is flowing to or from the metal at this point, the potential at the tubulus mouth in ontact with the surface must be different from that at the other vhich remains a short distance from the surface; a deflection will be egistered on the micro-ammeter, and its sign will indicate whether the oint is anodic or cathodic.

Thornhill worked with dilute salt solutions (N/1000 sodium chloride), vhich produced a rather different distribution of attack from that obtained t higher concentrations. After some initial irregularities, the electrical distribution became stabilized with the main cathodic zone extending along the top of the meniscus and the main anodic zone along the foot of the meniscus. Thornhill found that, even in the opening stages of irregular distribution, the principal cathodic zone was always above the anodic zone and that at any moment *attack was only observed at those points which the electrical apparatus showed to be anodic*; points which were *not being attacked* were found to be either *cathodic* or *neutral*. This seems definitely to establish the electrochemical mechanism.

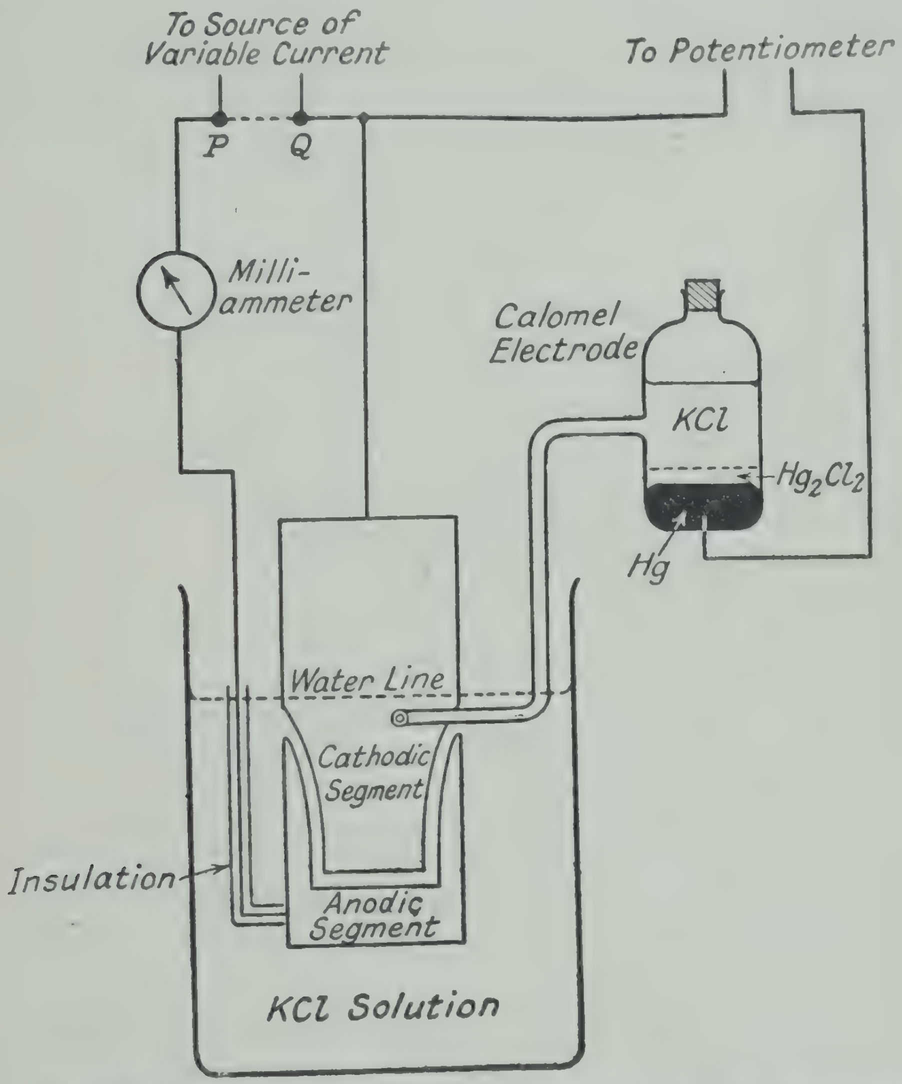
To Source of Variable Current
To Potentiometer
P
Q
Milli-ammeter
Calomel Electrode
KCl
Hg_2Cl_2
Hg
Water Line
Cathodic Segment
Insulation
Anodic Segment
KCl Solution

Fig. 26.—Principle of Measurement of Corrosion Current on Iron partially immersed in Potassium Chloride Solution (T. P. Hoar and U. R. Evans).

Quantitative Verification of the Electrochemical Mechanism o Iron. The first accurate measurements of the currents flowing over th surface of a simple corroding specimen were carried out at Cambridg by Hoar,[52] using a steel prepared for the purpose by Hatfield, whic regularly furnished the ideal distribution (Fig. 22 (left), p. 30) in potassiu chloride solution. Hoar was thus able to cut a specimen along the line which he knew would come to represent the boundaries of the anodi area, when later the specimen was immersed vertically in the solution after carefully covering with wax the new edges produced by th cutting, he mounted the two parts in their proper relative positions in containing vessel, but connected to the two terminals of a milliammeter the arrangement was that shown in Fig. 26, with P and Q joined. Th

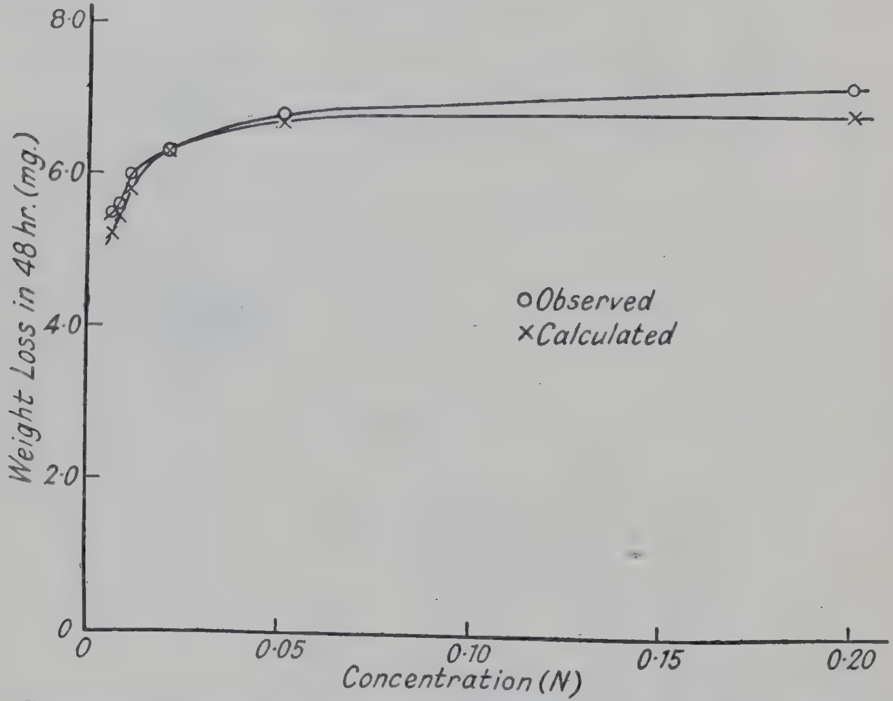

Fig. 27.—Corrosion of Iron in Potassium Chloride Solution (*a*) observed by weigh loss, (*b*) calculated from purely electrical data (U. R. Evans and T. P. Hoar).

liquid was then poured in and the current passing was measured; this was found to correspond—in the sense of Faraday's law—to the corrosion velocity as obtained by loss of weight.

Hoar performed further experiments in which currents of known strength were applied from an external source joined up between P and Q. For each value of the applied current, he measured, by means of a calomel electrode and potentiometer (p. xxix), the value of the P.D. between metal and liquid at the cathodic zone situated near the water-line. Owing to polarization, this P.D. dropped as the applied current was increased, and curves could be plotted showing the relation between P.D. and current. It thus became possible to measure the current flowing on *uncut* specimens, because the P.D. could be measured on the water-line zone and the corresponding current read off from the curves. Division by Faraday's number gave the corrosion velocity, and the values thus obtained at various concentrations (Fig. 27) showed excellent agreement with the experimental values obtained by loss of weight. No arbitrary constant was involved in these comparisons; if the corrosion had not been electrochemical in character, there would have been no reason to expect that the two sets of numbers would even be of the same *order* of magnitude.

Hoar's experiments—just quoted—refer to corrosion set up by differential aeration on partly immersed specimens. Another comparison has been carried out on corrosion produced by sodium bicarbonate solution at a scratch-line. Sodium bicarbonate is peculiar in that its dilute solutions are highly corrosive to steel, although concentrated solutions cause no attack; this is probably due to the reduction in the solubility of ferrous bicarbonate by the presence of excess of $(HCO_3)'$ ions, which permits the formation of protective films in concentrated solutions. At intermediate concentrations, behaviour depends on the previous history of the metal. An abraded surface, exposed to air for some time before the bicarbonate solution is applied, is not attacked; but if a scratch-line is traced on the surface just before the liquid is applied, rusting sets in along that line. Mears,[110] in his statistical studies, found that the probability of corrosion by 0·07M sodium bicarbonate (measured by the proportion of the scratch-

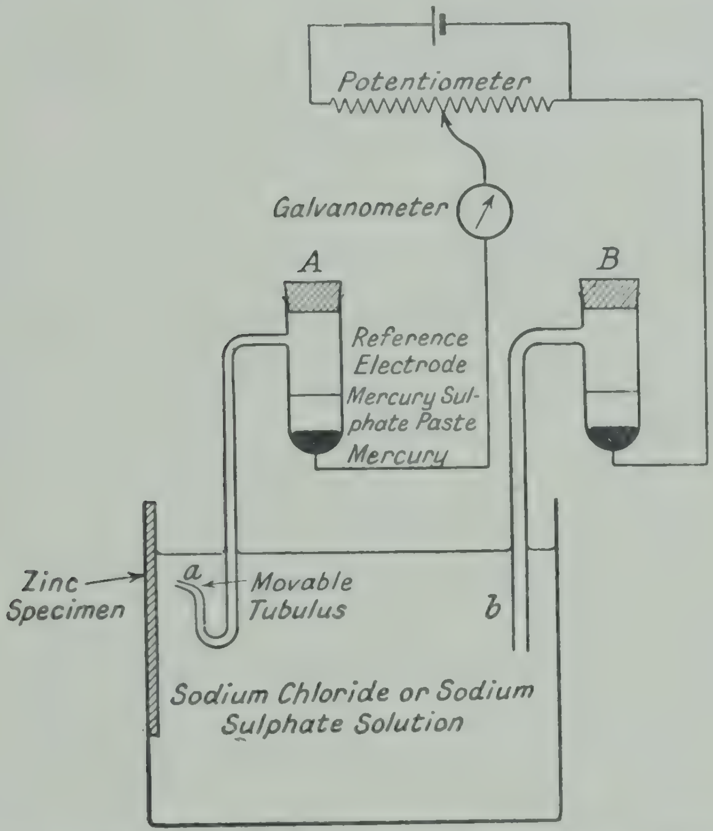

FIG. 28.—Apparatus for Exploring the Distribution of Potential around Corroding Zinc (J. N. Agar and U. R. Evans).

lines producing rust) fell off steadily as he increased the period of exposur to air before application of the liquid.

If a single fresh scratch-line is made on a surface which has long bee exposed to air, and a piece of filter-paper soaked in dilute sodium bicarbon ate is applied, a rust stain is produced along the length of the scratch-lin The author,[44] by means of a special dielectrode, showed that an electri current was really passing between the scratch-line as anode and th surrounding region as cathode. Later, Thornhill [143] succeeded in cal brating the apparatus and thus obtained an accurate measurement o the current. At the outset, the current corresponded to the corrosio velocity on the assumption that the iron was passing into solution in th ferrous condition ; later it increased in relation to the corrosion—whic was explained on the supposition that, when once a quantity of ferrou bicarbonate had accumulated, it underwent anodic oxidation to the ferri condition, thus accounting for the surplus current.

Quantitative Verification of the Electrochemical Mechanism o Zinc. In the case of zinc partly immersed in chloride or sulphate solution Agar [1] obtained a measure of current by studying the distribution o potential in the liquid. He used (Fig. 28) a single electrode supporte in a stand, provided with screw-gear which allowed motion in thre directions at right angles ; the apparatus carried scales which indicate the exact position assumed by the tubulus tip. The electrode was joine through a potentiometer to another electrode fixed at a distance from th metal. Agar traced the shape of surfaces upon which all points wer at the same potential ; the " equipotential " curves of Fig. 29, whic refer to N sodium chloride, represent the intersection of such surface with the plane of the paper. Since the equipotentials must be crowde together if the current is strong, but must lie far apart if it is weak they can be used for the calculation of current strength. If two equipotentials differing by $\varDelta V$ are separated by distance G, the curren flowing from one to the other is approximately $\kappa A \varDelta V/G$ where κ is th specific conductivity of the liquid, and A the mean area of the two surfaces Considering equipotential surfaces extending for 1 cm. along the waterline, the area of any such surface is L sq. cm., where L is the length o the equipotential lines, such as those shown in Fig. 29. If two such lines, separated by a mean distance G, have lengths L_1 and L_2, the current per centimetre length of water-line will be approximately

$$\kappa\frac{(L_1 + L_2)}{2}\cdot\frac{\varDelta V}{G}$$

The currents obtained by measuring L_1, L_2, $\varDelta V$ and G were found to be sufficient to account for the whole of the attack leading to a loose corrosion product. A small amount of adherent product formed above the water-line may be connected with upward creepage of alkali from the cathodic zone. Agar's work was interrupted in 1939 by the outbreak of war, but had reached a point at which it furnished important quantitative evidence for the electrochemical mechanism of the reactions studied.

The manner in which the corrosion current depends on the polarization characteristics of the metal and oxygen and on the resistance of the circuit is discussed on p. 71 in connection with acid attack.

Anaerobic Action of Water on Iron. Considerations of energy indicate that iron should be capable of displacing hydrogen from water even in the absence of oxygen. The iron will pass into solution as ferrous hydroxide. As the ferrous ion concentration increases, the potential of the iron will move in the positive direction; at the same time the hydroxyl ion concentration will increase, causing the potential of hydrogen to move in the opposite direction. Thus the E.M.F. available for corrosion declines.

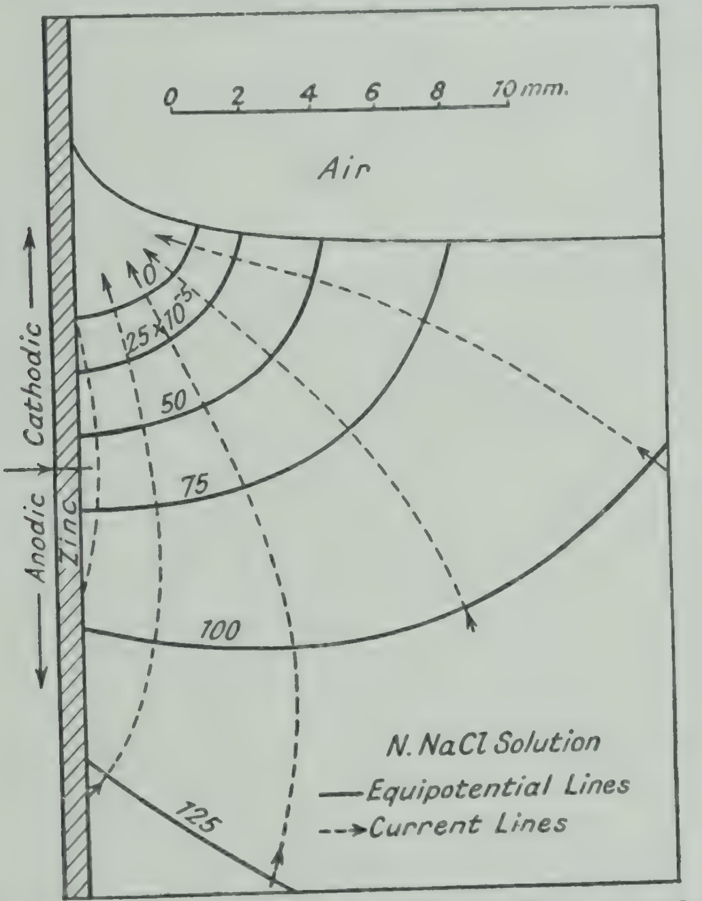

FIG. 29.—Potential Distribution and Current Flow around Zinc in N Sodium Chloride Solution (J. N. Agar and U. R. Evans).

But even when the solution has become saturated with ferrous hydroxide, there remains a small residual E.M.F. to drive the exchange process. If a salt is present in the water, say sodium chloride, the ferrous hydroxide will arise by interaction between the soluble anodic product, ferrous chloride, and the soluble cathodic product, sodium hydroxide, and any precipitate will be formed at a sensible distance from the seat of corrosion, so that no stifling will occur; the corrosion can then proceed indefinitely, although much more slowly than if oxygen were supplied to the cathodic portion. Baylis [6] has shown that salts stimulate the anaerobic attack upon iron. If salts are not present, there is a better prospect that the reaction may ultimately stifle itself by producing a protective layer ferrous hydroxide (unless a trace of oxygen is present to convert it t ferric hydroxide at a distance from the metal, which will prevent stiflin as explained on p. 25). It happens, however, that ferrous hydroxid can decompose water, yielding magnetite and hydrogen,

$$3Fe(OH)_2 = Fe_3O_4 + 2H_2O + H_2$$

The change will only start here and there, but a nucleus of magnetit once formed, will continue to grow. Thus, because the reaction occur at a few points only, the magnetite will form a loose, granular deposi instead of a protective film ; wherever magnetite appears, the concentration of ferrous hydroxide must locally fall below the solubility limit and the maintenance of a completely protective film of ferrous hydroxid becomes impossible ; thus a very slow attack by pure water on iron i the absence of oxygen can continue indefinitely. This anaerobic corrosio of iron by water has been recorded by Thompson,[141] and also by Corey and Finnegan.[25]

Electrochemical Action with Applied E.M.F.

General. In the cases of electrochemical action hitherto considered, the metal has provided its own E.M.F. The rate of attack is often limited by the rate at which oxygen, the cathodic reactant, can reach the cathodic area.* Where an E.M.F. is applied from an external source, much greater rates of anodic attack become possible.

Consider, for instance, two iron plates dipping into sodium chloride solution and connected to a dynamo or external battery. The rate of corrosion of the anode is, in the absence of passivity (see below), proportional to the current flowing, and may be very rapid. On the other hand, the cathode will suffer less corrosion than in the absence of external E.M.F., and, if the cathodic current density is sufficient, may be protected completely (see p. 49).

Factors Deciding between the Formation of Salts or Oxides on an Anode. Any aqueous salt solution contains, in addition to anions such as SO_4'' or Cl' (according to the salt chosen), a small concentration of hydroxyl ions (OH') due to the dissociation of the water. It is important to know whether the anodic product will, in effect, be a soluble salt (sulphate or chloride), or whether it will be a sparingly soluble oxide (or hydroxide), since in the latter case even electrochemical attack may be stifled ; in the present section, the word " oxide " includes " hydroxide " also.

Consider [53] two metal electrodes in a slightly acid solution of the sulphate of the same metal ; if a certain quantity of metal passes into solution at the anode as soluble sulphate, and the same quantity of metal is deposited on the cathode, no chemical work is performed, but merely transfer of metal from anode to cathode ; under reversible conditions, therefore, the smallest possible E.M.F. should suffice to force an infinitesimal current through the cell. But if the current were to deposit solid oxide on the anode, a system richer in free energy would be produced, since the acid liquid could subsequently dissolve the oxide spontaneously, with a decrease of free energy; the production of solid oxide on the anode would require a definite E.M.F. to supply this energy. Thus, at very low E.M.F.s, the production of soluble sulphate is the only reaction possible, provided that the liquid is sufficiently acid to ensure that solid oxide is not a stable phase. If the liquid were mildly alkaline, so that the oxide could remain undissolved as a stable phase, then the same argument would predict that a solid oxide film will be formed at very low current densities, and that the electrode will become " passive " and largely cease to dissolve. Thus corrosion may be looked for in acid solutions, whereas passivity may be expected in alkaline solutions, unless the oxide of the metal under study is soluble in alkali of the concentration present. The factor deciding between activity and passivity, at least at low current densities, is the power of the solution to dissolve (however slowly) the metallic oxide.

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* Cases of attack by acid and alkali which proceed rapidly in absence of oxygen are discussed in Chapter III.

Many salts added to pure water give no clear solution, but suffer hydrolysis and precipitate an oxide, hydroxide or basic salt. A clear solution can only be obtained if sufficient acid is added to reduce the p_{H} below a certain value. According to the rule suggested above, solutions more acid than this value should permit of free anodic corrosion, whereas at higher p_{H} values, anodic action is likely to coat the anode with an oxide film, leading to passivity.

The rule just enunciated refers to low current density. A high current density involves an abnormal drainage of electrons from the anode surface, and, in the case of a metal forming more than one series of compounds, can lead to the production of ions of higher positive charge than those produced at low current density. A low E.M.F. applied to a cell consisting of two vertical iron plates in a sodium chloride solution will yield colourless ferrous chloride at the anode. If the major part of the anode is covered with wax, with the exception of one narrow scratch-line, the local anodic current density may become very high, and the potential may be raised by polarization to such a value that three electrons, instead of two, are abstracted from every iron atom; a wisp of yellow ferric chloride may then be seen descending from the scratch-line. Similarly, at low E.M.F.s a lead anode in sulphuric acid becomes covered with a barely visible lead sulphate coating which causes the current to fall off with time; but if the E.M.F. applied is sufficient, a slow attack continues, yielding quadrivalent instead of divalent lead compounds, so that a puce-coloured covering of lead peroxide appears on the anode. Again, chromium dissolves in an acid solution at low current density to give a blue solution containing divalent ions, but at high potentials it dissolves in the hexavalent condition, yielding yellow chromic acid.

Passivity on a Horizontal Anode. It may often happen that a metal dissolves freely at low current densities, giving a soluble salt, but at high current densities passivity supervenes, owing to the formation of an oxide film over the anode surface ; when once this film has appeared, most of the current which continues to pass is devoted to the production of oxygen. Under very stagnant conditions, even a low current density can ultimately bring about passivity ; but the time needed for active dissolution to give place to passivity increases as the current density diminishes. This was shown by W. J. Müller,[115] who used a horizontal anodic surface protected from chance stirring by a hood (Fig. 30 (*a*)). With a vertical anode (Fig. 30 (*b*)), particularly if there is rapid movement of the liquid over it (Fig. 30 (*c*)), conditions are less favourable to passivity, which will only set in if the current density is high.

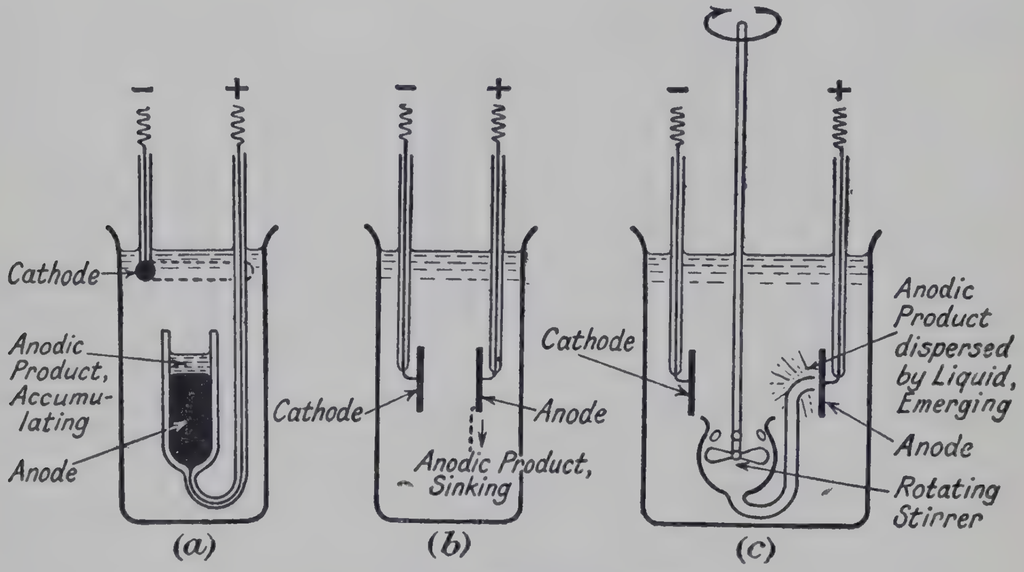

Fig. 30.—Electrolytic Cells.

(*a*) With horizontal anode protected from chance stirring (W. J. Müller's Method)—an arrangement favouring passivity.

(*b*) With vertical anode, allowing the heavy anodic products to sink—an arrangement less favourable to passivity.

(*c*) With a rapid movement of the liquid over the anode (Shutt and Walton's Method)—an arrangement preventing passivity except at high current densities.

Müller's extensive experiments with " protected " anodes (Fig. 30 (*a*)) showed that the first stage in " passivation " is often the production of crystals consisting of a simple salt of the metal. Consider an iron anode in dilute sulphuric acid. At first ferrous sulphate solution is formed over the anode surface and accumulates, since the stagnant conditions preclude its dispersal. Sooner or later the solution must here become so supersaturated with ferrous sulphate that the salt begins to crystallize out ; Müller detected the tiny crystals (in this and similar cases) by means of a polarizing microscope. As the crystallization extends, an increasing fraction of the anode surface is covered up, and (for a fixed applied E.M.F.) the current flowing decreases, although the current density on the portion remaining uncovered may actually increase. Since all the time hydrogen ions are migrating away from the anode, the solution in the interstices of the crystalline deposit probably ceases to be acid, and conditions are established under which the expected reaction, according to the rules stated above, should be the production of an oxide film. So soon as the oxide film appears over the surface, the dissolution of metal is obstructed, and any further current passing is devoted to the production of oxygen; the gas-evolution then disperses the little crystals of sulphate, which either dissolve or are swept away. The stirring connected with the evolution of gas must bring back acid to the metallic surface, but (provided that the anodic current density is high enough to ensure that there is no reduction of ferric oxide to the ferrous state) the anode remains passive, since the rate of direct dissolution of sesquioxides by acid is always slow (p. 42).

Passivity on a Vertical Anode. At low current densities, a vertical anode never becomes passive at all, since the heavy anodic product sinks down (Fig. 28 (B)), and supersaturation is not produced. Above a certain limiting current density, however, passivity becomes possible. If the current density employed is well above this limit, the passivity, when once it has set in, persists indefinitely, and the passive anode behaves as an unattackable electrode, approaching platinum in behaviour and potential, although a very slow rate of corrosion (representing perhaps 1% of the current) can often be detected. If the current density has been only just sufficient to bring about passivity, then the restoration of acid conditions brought about by the stirring effect of the oxygen bubbles may cause the anode to become active again, and we thus obtain fluctuations to and fro between the active and passive states. This *periodicity* has been studied in detail by Hedges.[74] In general it is found that

(1) *low* current densities produce *active corrosion*;
(2) *intermediate* current densities produce *periodicity*; and
(3) *high* current densities produce *passivity.*

At a given current density the presence of chlorine ions favours active corrosion; this is true not only of iron, but of most other metals. It is uncertain how far this is due to the high solubility of chlorides, and how far to the ability of chlorine ions to penetrate and undermine protective films. Generally, a metal tends to become passive if subjected to anodic action in the presence of ions which produce sparingly soluble salts, and to remain or become active in presence of those which produce highly soluble salts. On iron, and all metals whose oxides possess a basic character and are soluble in acids, an acid reaction favours the active state, whilst an alkaline reaction will tend to maintain passivity. For metals like tungsten and molybdenum, where the main oxides have an acidic character (forming tungstates or molybdates), the reverse is true; such metals can suffer anodic corrosion in alkaline solutions at a rate determined by Faraday's law, whereas in acid solution passivity commonly sets in.

Behaviour of Ferric Oxide Films in Acid. At one time it used to be argued that the passivity produced on an iron anode in dilute sulphuric acid could not be due to an oxide film, since—it was urged—any oxide would be dissolved by the acid. Actually the liquid probably ceases to be acid along the anode surface before the film is formed, but in any case it is untrue to state that ferric oxide films are *quickly* dissolved by dilute sulphuric acid.

The author's experiments [41] on iron coated with *visible* oxide illustrate the essential facts. Freshly abraded iron was heated to produce first-order tints and tested in dilute acid; the colours quickly disappeared, suggesting that acid can destroy ferric oxide films. But then the experiment was repeated with iron heated to give thicker films, and it was now found that the acid caused the films to peel off, apparently by attacking the metal at their base. When once the oxide flakes were out of electrical contact with the metallic basis, solvent action practically ceased; indeed, they could be kept in M/10 sulphuric acid for eighteen days without losing their flake form. Evidently the *direct* solvent action of acid on ferric oxide is extremely slow, and the rapid destruction of the films when in electrical contact with the iron must be ascribed to the cells

Iron | Acid | Ferric Oxide

set up at cracks in the film. The iron exposed at each crack is the anode of the cell, and the ferric oxide, being the cathode, is reduced to the ferrous condition, and at once passes into solution as ferrous sulphate.* If this is the correct explanation, it should be possible to prevent the destruction of the film by the presence of an oxidizing agent. Experiments confirm this expectation. It was found that M/100 sulphuric acid containing chromic acid (M/10) produced practically no alteration to tinted iron, although M/100 sulphuric acid, in the absence of chromic acid, caused appreciable change in five seconds, and complete destruction of the earlier colours in one minute.

Another rational method of preventing destruction is to submit the tinted specimen as a whole to anodic treatment, thus preventing local cathodic action. Iron tinted to a first-order colour and subjected to anodic treatment from the moment of its introduction into the acid, suffered no change of colour and no corrosion; the specimen behaved as a passive anode, oxygen gas being evolved. An interruption of current for a fraction of a second was possible without dispelling passivity or destroying the colour; the evolution of oxygen recommenced when the current was turned on again. Longer interruptions of current destroyed the colour, revealing bright iron below, and ordinary anodic dissolution began when current was again applied. An anode heated to show second-order colours behaved similarly, but interruptions of current for fifteen seconds did not destroy the film completely, although they allowed attack on the iron to begin at certain points. A series of such interruptions, with intervening periods of current flow, produced complete undermining of the film, which peeled off in curling flakes; when once out of contact with the metal, the oxide film remained unchanged in the acid for hours.

Isolation of Films. The experiments just described suggested a method of isolating the invisible film which was believed to be present on untinted iron after it had been rendered passive by anodic treatment in dilute sulphuric acid at high current density. A specimen of clean (unheated) iron was subjected to anodic action in normal sulphuric acid at 6 volts; at first it suffered active corrosion, but soon became passive, oxygen gas appearing. If the circuit was now broken for a short time and restored, the anode was found once more to be active, and iron passed into solution; in due course passivity returned, and thus the iron could be made active and passive alternately.

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* Probably ferrous *ions* are formed, and pass directly into solution without intermediate production of *solid* ferrous oxide. Films on nickel (already divalent as NiO) and on aluminium (invariably trivalent as Al_2O_3) are only very slowly attacked by dilute acids.

The experiments were then repeated in a cell built on the stage of a microscope and furnished with a sloping anode. During the passive periods, the anodic surface remained bright; but when, after an appropriate interruption, the current was renewed, a series of horizontal shadow fringes passed upwards over the surface, due to the wrinkling of a thin surface film, which had been present in optical contact with the metal during the passive stage, but only became visible when the metal immediately below it was dissolved away. By timing the interruption at the suitable moment, it was possible to undermine the whole film, which frequently, as it peeled off from the anode, rolled up like a carpet into long tight microscopic rolls. Although mechanically flimsy, the films were chemically stable, and could survive an hour in normal sulphuric acid, except where particles of metallic iron adhered to them. These experiments showed that anodic passivity is due to a thin protective film, invisible on the metal, but perfectly visible when stripped from it. The rapid destruction of oxide films, and the accompanying loss of passivity, produced when metal is dipped into acid without applied current, is due *not* to the direct dissolution of the ferric oxide film (yielding ferric ions) but to its *reductive dissolution* (yielding ferrous ions).

Stray Currents

Corrosion of Buried Metal-Work caused by Tramways. The current needed to drive street tramways is generally picked up by the cars from overhead conductors, and returned to the rails; it is supposed to follow the rails back to the power station or transformer station. In practice (Fig. 31), part of the current sinks into the ground, travels along any pipes or cable sheaths which lead in an appropriate direction, later returning to the tramway rails (sometimes a different track). The fraction returning by this indirect path is small if the streets are well-paved and the ground dry; it is increased locally if salt is thrown on to the ground, either in summer by ice-cream vendors, or in winter by the tramway staffs (to prevent the freezing of points), and such practices should be discouraged. In so far as current returns via pipes or sheaths, two electrolytic cells in series are produced,

Steel Rails (anode) | Damp Ground | Steel Pipes or Lead Sheaths (cathode)

and

Pipes or Sheaths (anode) | Damp Ground | Rails (cathode),

causing corrosion of the rails at XX′ (which is not serious, since in any case rails require periodical replacement), and of the pipes or sheaths at AA′ (which may be very serious).

Calculations from Faraday's law show that 1 ampere flowing for a yea can destroy 20 lb. of iron or 75 lb. of lead, but on lead the effect is muc more disastrous than that number would suggest, since the attack dig in along grain boundaries and may perforate a sheath even when th weight of metal destroyed is small. In general, corrosion is likely t *start* at grain boundaries, where the atoms, being on two sides in touc with assemblages having different crystal orientations, are more easy t dislodge than at a point where an atom is surrounded on all sides b atoms of a single orientation. Considerations of energy might lead u to expect that in most metals the grain boundaries would be anodic t the grain interior. But in "natural" corrosion, any corrosion due t electrochemical action between the boundaries as anodes and the mai part of the adjacent grains as cathodes, is likely to stifle itself by th precipitation, at the grain boundaries, of the hydroxide or basic carbonat resulting from interaction of the anodic and cathodic products. I corrosion by stray currents, the anodic and cathodic regions may be som hundreds of yards apart, and such precipitation cannot stifle attack which continues to dig down along the grain boundaries, the corrosio product containing much chloride if salt is present in the ground; if th E.M.F. is sufficiently high, small quantities of lead peroxide may appear In the absence of stray currents, the attack is not directed specially on th grain boundaries, and the product consists largely of basic carbonate.

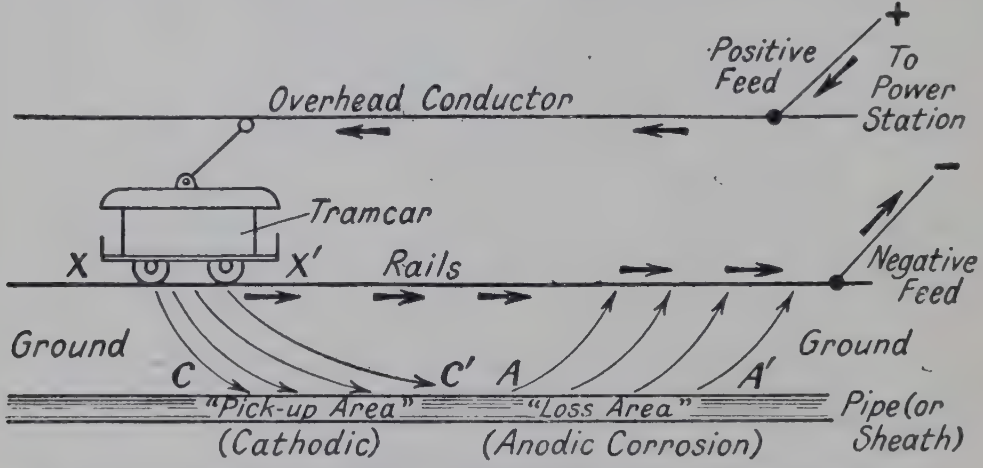

FIG. 31.—Corrosion by Stray Currents (the arrows show direction of flow of "positive" electricity).

On iron, corrosion by stray currents is not mainly directed upon grai boundaries, but it differs from "natural corrosion" in producing a hig concentration of chlorine ions at the anodic points where attack is mos severe; the electric current causes a migration of chlorine ions (whic are more mobile than most other anions) to the anodic points, and as the are not used up in the anodic process, the chlorine concentration at anodi points on steel pipes (and also on lead sheaths) often comes to be fa higher than that elsewhere in the ground or soil-water.

On both steel and lead, corrosion occurs in the anodic areas (AA′ i Fig. 31) where the "positive electricity" leaves the pipes or sheaths

On lead buried in salt ground, a different type of attack (not intergranular) is met with at the cathodic areas (CC′) where the sheaths are picking up current; the alkali formed by the cathodic reaction attacks the lead, a metal which possesses an oxide soluble in alkali. Iron—a metal which becomes passive in alkaline environment—is not attacked in the cathodic region.

A.C. produces less destruction than D.C., but its effect is appreciable, especially at low frequency, where a cathodic half-cycle is unlikely to undo completely the effect of the preceding anodic half-cycle. Moreover A.C., by alternate reduction and reoxidation, will sometimes render a film non-protective, and thus permit "natural" corrosion to proceed, where otherwise this would not occur.

Prevention of the Trouble. Damage to buried metal may be diminished by improved drainage and paving of the streets, by avoiding the use of salt on the ground and by careful electrical operating. Apart from these precautions, four methods have been used for preventing the trouble:—

(1) *Electrical Drainage.* The pipes or sheaths are connected (directly or through resistances and other electrical controlling devices) to the negative feeders, so as to make the whole system just cathodic to the ground. If no part of the pipe or sheath is anodic, there can be no anodic attack upon it by stray currents. Care should be taken not to make the metal strongly cathodic, or the current taken up will be increased, which may enhance the anodic corrosion of other pipes or sheaths not incorporated in the "electrical drainage scheme". Moreover, on lead sheathing in salt soil strong cathodic polarization ("overdrainage") may actually *cause* corrosion by the cathodically formed sodium hydroxide. The policy should be controlled by a joint committee representing all the interests (e.g. gas, water, electric power and telephone undertakings). Electrical drainage has given good results in certain Australian and Italian cities, but is not greatly favoured in Great Britain.

(2) *Insulating Bonds.* If the lead cable sheaths or pipes are interrupted by insulating gaps at appropriate intervals, the current passing along them is reduced and corrosion diminished. If, however, the number of insulating joints is insufficient, any current which does still flow will produce increased damage, since at each joint an electrolytic cell will be set up where the current leaves the metal to pass into the soil, and corrosion will be found on the anodic side of the gap; in water-pipes, the attack will occur inside, as the current will largely pass through the water. Used with judgment, this system gives excellent results. It is favoured by the Engineers of the British Post Office.

(3) *Sacrificial Bars.* If at the places where the current would normally leave the pipes, earth-bars of cheap iron or steel are provided which make good contact with the earth (being buried in beds of wet coke breeze if necessary), and if the rest of the pipe is covered with a protective coat (see p. 46), the current must leave by the earth-bars, which are consequently

rapidly attacked; they require replacement at intervals, but the pipes, which are more valuable, are spared. The system has given good results in one region in the English Midlands, where corrosion due to stray currents had previously caused trouble.

(4) *Protective Coatings.* Pipes are frequently covered with protective coats, based on tar, bitumen or other materials; lead cable sheathing is often coated with grease containing sodium silicate, or in special cases with rubber-wax. In its effect on stray-current corrosion, almost any coating applied to the cathode section is favourable, since it diminishes the amount of current picked up by the pipes or sheaths. In the anodic sections, however, a coating, if not complete, may make matters worse, since the whole of the current will escape at the discontinuities, and corrosion, thus localized, may be very intense. Coatings of high quality, however, can confer benefit.

In many districts, the replacement of tramways by trolley buses (with two overhead connections) has largely eliminated corrosion trouble due to stray currents.

Other Troubles arising from Stray Currents. In buildings where steel frames are surrounded by cement, considerable damage may be caused by stray currents if the cement contains chloride; the ferrous chloride formed anodically is precipitated by the alkali of the cement, causing a type of rust which occupies a larger volume than the iron destroyed in producing it, so that the expansional forces often rupture the cement, sometimes laying bare the steel. Some years ago this type of damage was frequently reported, e.g. where electrochemical processes based on salt solution were carried out in buildings of steel-and-concrete construction and fitted with circuits which permitted the escape of electric current. The trouble can generally be avoided by appropriate precautions.

At shipbuilding yards, it often happens that ships being fitted out in a basin have cables run on to them from land for welding or temporary lighting. If several ships are on the same circuit, the hulls will rarely be at the same potential, and current will pass from one to another through the sea-water, causing severe corrosion to whichever ship happens to be the anode; the attack is concentrated at gaps in the paint, and sometimes produces grooves recalling chisel-marks. The matter will not necessarily be rectified merely by joining the hulls together with a copper cable, since, although the copper is a better conductor than dock water, its cross-section is smaller, so that an appreciable fraction of the current takes the liquid path. It should usually be possible to avoid damage by suitable electrical planning.

Corrosion at Contacts between Dissimilar Metals

General. When two dissimilar metals in electrical contact are introduced into a corrosive salt solution, the anodic metal will, in general, suffer more corrosion, and the cathodic less corrosion, than if they were placed separately in the same solution. This principle is brought out in

Table VIII for couples of iron and a second metal in 1% sodium chloride, studied by Bauer and Vogel.[5]

TABLE VIII

Corrosion of Plates of Iron and a Second Metal in Electric Contact totally immersed in 1% Sodium Chloride (O. Bauer and O. Vogel)

Second Metal	Corrosion (Iron). mg.	Corrosion (Second Metal). mg.
Magnesium	0·0	3104·3
Zinc	0·4	688·0
Cadmium	0·4	307·9
Aluminium	9·8	105·9
Antimony	153·1	13·8
Tungsten	176·0	5·2
Lead	183·2	3·6
Tin	171·1	2·5
Nickel	181·1	0·2
Copper	183·1	0·0

Unalloyed aluminium is anodic towards alloys like duralumin and lautal which contain copper. At a junction with unalloyed aluminium, the alloy is often protected at the expense of the aluminium, although when both are disconnected, the alloy is the more rapidly corroded of the two materials. Likewise, on specimens of steel bolted to wrought iron and exposed five years in the sea at Plymouth by Friend, the steel was protected at the expense of the wrought iron, although disconnected specimens of wrought iron were corroded less than disconnected specimens of steel.

Stimulation by Direct Contact. If iron is joined to a cathodic metal like copper, the attack on the iron is usually stimulated, especially if the area of the second metal (copper) is large compared to that of the iron ; for the amount of oxygen reaching a large cathode will exceed that collected by a small cathode. Serious intensification of corrosion caused by the combination of small anode and large cathode will, however, only arise when the control is "cathodic", the current being determined mainly by events at the cathodic metal (in this case, by the rate of arrival of oxygen). If the current were limited by the existence of a nearly continuous insulating film on the anodic metal, which might occur if the anodic metal were stainless steel ("anodic control"), the cathode-anode ratio would become less important.

In cases where the control is purely cathodic, a curious result is obtained. Whitman and Russell[162] compared the corrosion of bare plates of steel with similar steel plates in which three-quarters of the surface was coated with copper. The total attack was found to be the same in both cases, but on the coated plate it was concentrated upon the bare quarter, where the intensity of attack was consequently four times as great. The reason is clear. The copper received the oxygen which (in the absence of the coat) would have reached the underlying iron; being a cathode, it was not itself attacked, but passed on the corrosion to the anode, the bare iron; in other words, the copper acted as a catchment area for the iron. The catchment area principle must, however, not be pushed too far; had 99·9% of the iron been coated with copper, the attack on the tiny bare area would not have been 999 times as intense as that of an uncoated plate, since in this extreme case the anodic polarization, and the resistance of the bottleneck approach to the anode, would have restricted the current.

Many cases of serious attack through contact between dissimilar metals have been reported from industry and structural engineering. Aluminium alloys—resistant to many liquids owing to the presence of an alumina film which is itself too bad a conductor to act efficiently as a cathode towards the metal exposed at discontinuities in it—may become rather rapidly attacked by salt water at contact with copper. The attack produced by a globule of mercury resting on wet aluminium is due to a different cause, the film formed on amalgamated aluminium being non-protective; the breaking of a mercury thermometer in an aluminium vessel at a brewery has led to rapid perforation.

Indirect Stimulation. Serious consequences are sometimes met with where copper pipes and galvanized tanks or cisterns have been used together in a domestic water system. Rapid failure of the galvanized vessels has often been reported, and was at one time attributed to a cell with the copper as cathode and with the zinc or iron as anode. An investigation by Kenworthy [94] has shown that the trouble is due *not* to this *macroscopic* cell, but to numerous *microscopic* cells. Waters containing free carbonic acid act on copper, at a rate insufficient to damage the copper pipes, but sufficient to take up traces of copper bicarbonate, and thus deposit metallic copper on the galvanized iron (metallic zinc and copper salt give metallic copper and zinc salt). Little corrosion cells of the type zinc | copper (and later iron | copper) are set up, with disastrous results. Comparing two housing estates supplied with the same water, Kenworthy states that on one estate, where copper pipes were used with galvanized tanks, 50% of the installations failed in four years, although on the other estate, where both pipes and tanks were galvanized, there were no failures. He mentions two other neighbouring estates *both* fitted with copper pipes and galvanized tanks; on one, employing a water containing 4·1 p.p.m. free carbonic acid (which took up 0·32 p.p.m. of copper) *every* installation failed in four years; on the other estate, supplied with a less cuprisolvent water (1·1 p.p.m. free carbonic acid, taking up only 0·03 p.p.m. of copper), no failures were reported. He suggests as a remedy reduction of the cuprisolvency by lime additions or by aeration, which would remove much of the free carbonic acid.

Variable Polarity. Noble metals like silver and copper are cathodic to iron in nearly all liquids; base metals like zinc and aluminium are anodic to iron, at least if freshly abraded. Metals like tin and lead, which stand close to iron in the Potential Series (Table I, Endpapers), display a variable polarity; the presence of an oxide film on the one metal may render it cathodic, whereas the presence of a substance in the water forming complex ions with one metal may make it anodic; when a small current is passing in one direction, vigorous aeration of the metal functioning as anode often reverses the flow.

Tin behaves as cathode to iron in hot distilled water, but as anode in solutions of many organic acids, such as occur in fruit juice. Thus fruit preserved in canisters of tin plate (steel coated with a thin tin layer usually interrupted by pinholes) has little action on the steel exposed. The tin gives protection in two ways, (1) by direct cathodic protection at the expense of the tin, which suffers enhanced attack, (2) by the tin salts thus formed retarding the attack on the steel, probably by fixing in stable form the sulphur which would stimulate corrosion—as explained on p. 69; (in some circumstances, copper or molybdenum in the steel acts in the same way). Hoar [79] studied the corrosion of plates of tin and steel immersed in citric acid separately and in contact, and found a considerable increase in the attack on the tin when they were put into contact; the increase corresponded (in the sense of Faraday's law) to the current which was found flowing between them. There was a diminution in the corrosion of the iron, which in air-saturated solutions also corresponded to the current. Under anaerobic conditions, where attack of the hydrogen-evolution type was still possible, the diminution far exceeded the equivalent of the current; this additional protection was attributed to inhibition by the tin salts produced by attack upon the tin anode.

Although freshly abraded zinc is at ordinary temperatures strongly anodic to iron in all ordinary waters or solutions, the polarity gradually reverses at high temperatures. Kenworthy and Smith [95] found that, whereas a plate of galvanized (zinc-coated) iron, placed in cold water, suffers no corrosion of the iron exposed at the cut edges, a similar protection of exposed iron does not occur in hot water; this should be remembered in planning hot-water systems, where it is clearly important that the steel basis should nowhere be exposed. A similar reversal of polarity has been reported at ordinary temperatures, but it comes about much more slowly, and there is doubt as to whether it occurs under all conditions. In any case, it is always possible that, during the period whilst the iron is still the cathode, a protective film (zinc hydroxide, or calcium carbonate if the water is hard) may be formed on the exposed iron—in which case protection may continue even after the reversal of polarity.

Mechanism of Cathodic Protection. Hoar [79] pictures cathodic protection (e.g. of iron by tin) as follows. The cathodic parts of the iron surface can evolve hydrogen or reduce oxygen (to OH') at a limited rate. In an uncoupled specimen, this must be equivalent to the rate of corrosion of iron at the anode. If iron is coupled to a tin anode, part of the anodic attack falls on the latter, leaving less for the iron.

This is probably the main mechanism of protection in ordinary cases, but it is certain that, in some liquids, cathodic action can lead to a film or inhibitive product—and that these events can contribute to protectio For instance, if iron is made a cathode in a hard water rich in calciu bicarbonate, the alkali (calcium hydroxide) produced at the cathode wi interact with the calcium bicarbonate to throw down a film of calciu carbonate on the cathode. Or again, if steel is joined to zinc in a wate containing a zinc salt (perhaps formed through anodic attack on the zinc) the cathodic reaction may throw down a zinc hydroxide film over th steel. In both cases, the film can confer protection after the current ha ceased to flow, since any iron salts formed will be precipitated by th calcium carbonate or zinc hydroxide (in presence of oxygen) as a clingin —and therefore protective—form of rust.

Again, in a sodium salt solution, the sodium hydroxide formed at th cathode is an inhibitor and helps to prevent attack—so long as it is no dispersed. In such a solution, the author found that the cathode curren needed to protect a vertical rod of smooth steel was *diminished* if a scre thread was cut in the surface—despite the increased area to be protected the grooves helped to avoid the dispersal of the alkali.

Dissimilar Metals on Ships. Modern ships, although built of stee plates, are usually fitted with bronze propellers, which in their rapi rotation in aerated sea water receive an inexhaustible supply of oxygen Consequently, even if the area of the propellers were small compare to that of the ship, they might act as efficient cathodes; in practice since the greater part of the plates will be covered with paint (an sometimes with mill-scale), the anodic attack will be concentrated o the points where the paint (and scale) has been damaged. It is hel by some authorities that the corrosion met with on ships at breaks in th paint is largely due to the cell Steel | Bronze. Large plates of zinc ar usually fixed around the propeller shaft to counteract this effect, and t confer protection on the propeller itself. There is difference of opinio as to how far they are effective, and indeed as to whether the bronz really plays the destructive rôle attributed to it.

Zinc as Protection to Aluminium. Although zinc stands abov aluminium in the Potential Series, it behaves anodically owing to th oxide film on the aluminium. Zinc contact pieces have proved effectiv in stopping attack on aluminium cooling jackets and cooling coils i industry. Squares of zinc have given successful protection to duralumi wing-tip floats on flying boats. The protection often extends to surprisin distances.

Cathodic Protection with Applied E.M.F. Instead of using zinc i is possible to provide cathodic polarization by means of current flowin from an unattackable anode (composed, for instance, of carbon); the anode and the metal to be protected are joined to the two poles of a dynamo. Attempts to apply such electrochemical protection to vessels of complicated shape, such as boilers and condensers, have had limited success, since it is difficult to obtain the necessary cathodic current density at all parts of the surface. For simple forms, such as steel water-storage tanks, cathodic protection has been used in America with satisfactory esults, and to some extent seems to be displacing painting. Anodes of raphite or stainless steel are fixed in the water, the tank itself being the athode.

Another American development is the auxiliary protection of long ipe-lines against "natural" soil corrosion, which occurs even in the bsence of stray currents. To protect the whole surface of a pipe-line y electrochemical means would be expensive, but, if the pipe is coated vith paint or other composition, so that it only remains to protect the teel at defects in the coating, the power cost is much smaller; in some listricts the current is cheaply generated by dynamos driven from vindmills.

However obtained, a cathodic current, if applied in excessive strength may be deleterious to painted surfaces, since cathodically formed alkali can cause softening or peeling of the coat (p. 157).

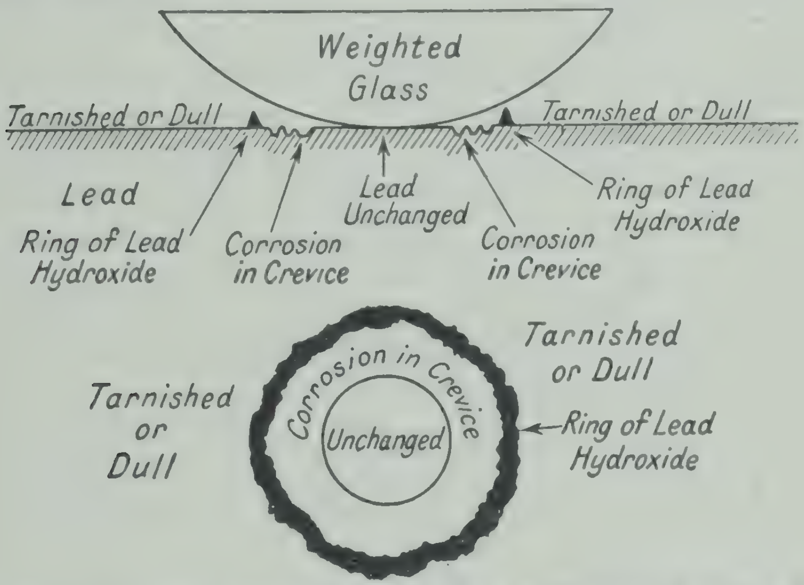
Weighted Glass
Tarnished or Dull
Tarnished or Dull
Lead
Lead Unchanged
Ring of Lead Hydroxide
Ring of Lead Hydroxide
Corrosion in Crevice
Corrosion in Crevice
Tarnished or Dull
Tarnished or Dull
Corrosion in Crevice
Unchanged
Ring of Lead Hydroxide

FIG. 32.—Corrosion produced on Lead in a Chloride Solution where a Lenticular Glass rests upon it.

Crevice Corrosion

General. Although no surprise has ever been occasioned by corrosion occurring at contacts between dissimilar metals, considerable mystification was at one time felt at the intense attack sometimes noticed where non-conducting substances pressed against metal. The explanation is to be found in the fact that where a "foreign body" (whether a glass rod, a stone, or a piece of fabric) rests against metal, an inaccessible cranny is formed in which replenishment of certain substances can take place only slowly.

Lenticular Glass on Lead. One case studied by the author[34] is that of a lenticular glass resting on a horizontal lead plate below the surface of potassium chloride solution (Fig. 32); alternatively a lenticular piece of cast lead can be placed in a porcelain dish containing the same solution. Over an annular area around the centre the lead suffers marked

OD TECHNOLOGICAL RESEARCH

attack ; beyond this comes a ring of lead hydroxide, outside which th lead, although dulled or tarnished, remains unattacked. This is explain by the fact that oxygen is less easily replenished in the annular crevi than elsewhere, and consequently anodic attack occurs here, yielding lea chloride, which, interacting with the sodium hydroxide formed at th better aerated cathodic regions, produces the ring of lead hydroxid Other metals show similar phenomena. A brass plate leaning against glass rod in sodium chloride solution often suffers a line of corrosi along the cranny between glass and metal.

Crevice Corrosion produced by Drops. Interesting effects we also obtained with drops of carbon tetrachloride placed on steel immerse in salt water, or on aluminium immersed in N/10 hydrochloric acid (Fig. 33

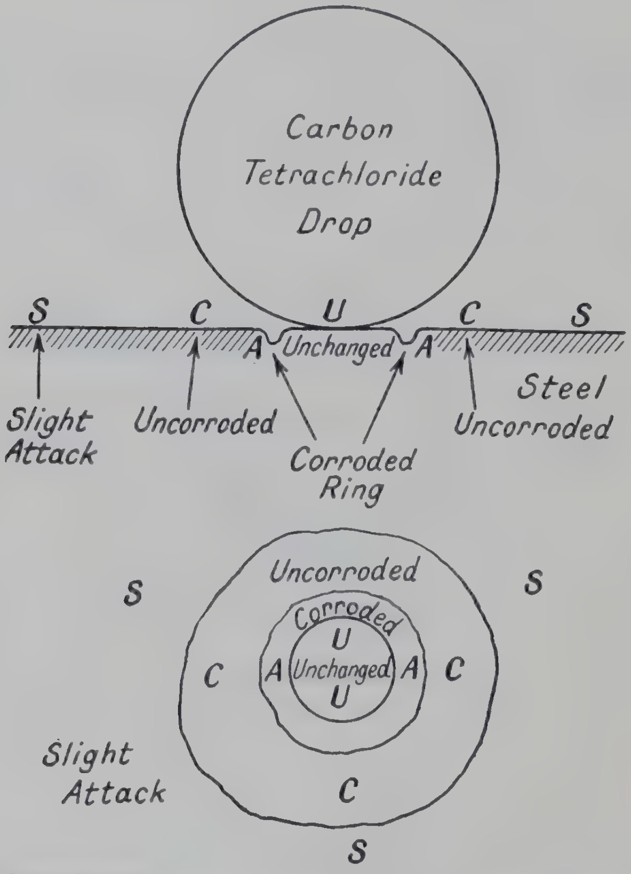
Carbon
Tetrachloride
Drop
S
C
U
C
S
A
Unchanged
A
Steel
Slight
Attack
Uncorroded
Corroded
Ring
Uncorroded
S
Uncorroded
S
Corroded
U
C
A
Unchanged
A
C
U
Slight
Attack
C
S

FIG. 33.—Attack set up Around a Drop of Heavy Inert Liquid.

Intense corrosion occurred over an annular region, but the author' measurements showed that in the first case the total attack was no increased by the placing of the drop on the steel ; indeed, it was slightly diminished ; the intensification was due to redistribution of the attack since the corroded ring (A) produced by the crevice was surrounded by a larger area (C) which suffered no attack at all.

Crevice Corrosion in Liquid containing an Inhibitor. In the case of iron, crevice corrosion is most often produced when enough inhibitor has been added to the liquid to bring conditions near to the oundary dividing passivity from corrosion. For instance, sodium arbonate solutions, if very dilute, produce corrosion, whilst higher oncentrations lead to passivity (cf. p. 35). On a certain steel used in the uthor's laboratory by Mears,[109] the borderline came about 0·05N, and vhen, in liquid of that concentration, a series of horizontal glass rods vas laid resting on a series of horizontal steel rods (the axes of the two series being at right angles to each other), it was found that corrosion was generally produced at the crevice between steel and glass, but not elsewhere. The reason is that inhibition involves a consumption of inhibitor see p. 136). Since at the cranny the inhibitor will be replenished less quickly than elsewhere, the probability of corrosion developing in the cranny area is greater than that of development at any area *of the same size* outside the crevice. Nevertheless, the corrosion does not invariably appear in the cranny. It will not occur if there chances to be no susceptible spot within the cranny area; nor will attack develop within the cranny if there happens to exist, just outside the cranny, an *exceptionally* susceptible spot which develops anodic attack (despite the good supply of inhibitor), and then confers cathodic protection on the cranny area itself.

Mears found attack at points where steel rods rested on other steel rods (arranged at right angles), and the frequency of attack was then actually greater than in the case of glass rods laid on steel. This was an important result, since it disposed of an alternative explanation of corrosion at steel-glass contacts—namely that films cling to glass in preference to steel, thus leaving the metal bare; there is no reason why a film should desert one steel rod in favour of another.

Attack at Crannies in Industrial Plants. Corrosion is sometimes noticed in badly designed chemical plant, particularly at places where heating coils or the like come close together. Austenitic stainless steel, a substance wonderfully resistant when a trace of oxygen is present, is liable to break down under anaerobic conditions, such as may exist at inaccessible corners. In designs likely to produce attack at anaerobic points, it may sometimes be better to choose a material like Monel Metal, the corrosion of which diminishes with diminishing oxygen concentration, rather than stainless steel, where the passivity may break down when the last trace of oxygen is removed. Clearly for highly aerated conditions, the opposite choice may be indicated.

Corrosion at inaccessible anaerobic spots may in some cases be due to sulphate-reducing bacteria (p. 87), which flourish at such places.

Cranny Corrosion on Aircraft. Aluminium alloys are also liable to suffer crevice attack in marine environments, although resistant to attack on the free surface; this is attributed by most authorities to differential aeration; the voluminous character of the corrosion product (if precipitated within the cranny) may cause serious bulging.

Cranny Corrosion in Structural Steelwork exposed to the Atmosphere. Probably the main reason why atmospheric corrosion occurs rapidly in crevices left between steel plates is that moisture is retained there long after it has dried up on the external surfaces. The dangerous feature of such crevice corrosion is that the rust occupies much larger volume than the steel destroyed in producing it ; the effe is similar to that of a wedge driven in between the plates, forcing the apart. A case is known of the failure of a line of rivets holding two plat together on a bridge ; these had been spaced too widely apart, so th they snapped one after the other by the lever action of the rust forme in the crevice. It is most important to fill up all such crevices ; red lea paste is suitable for steel, and certain mixtures containing zinc chroma for aircraft alloys.

The evidence for the electrochemical mechanism of corrosion, wit a description of a new experimental method of measuring corrosio currents, is collected in a paper to be delivered by the author to th International Congress of Pure and Applied Chemistry in July 1947.

CHAPTER III

CORROSION BY ACIDS AND ALKALIS

Action of Non-Oxidizing Acids

Mutual Replacement of Metals. The attack upon a metal by a non-oxidizing acid is essentially a replacement of hydrogen by the metal in question. It may be better understood if some other cases of mutual replacement are first considered.

When a base metal is placed in the solution of a salt of a more noble metal, i.e. one standing above it in Table I (Endpapers), mutual replacement usually occurs. Thus metallic iron placed in a copper sulphate solution becomes coated with metallic copper, iron sulphate appearing in solution; zinc placed in lead acetate produces a tree of metallic lead; copper precipitates mercury from a salt, and so on. Exceptions are met with where a resistant oxide film is present, and if the normal potentials of the two metals stand close together, the replacement may be incomplete and reversible. Tin throws out metallic lead if placed in a lead salt solution, but lead deposits tin from a tin salt solution; in both cases, replacement ceases when the liquid contains tin and lead in the ratio 2·98:1, since towards such a solution the potential of both metals is the same, and equilibrium

$$\mathrm{Sn}^{\cdot\cdot} + \mathrm{Pb} \rightleftharpoons \mathrm{Pb}^{\cdot\cdot} + \mathrm{Sn}$$

is established.

Hydrogen Evolution. If a metal is placed in acid, contained in a closed vessel, replacement of hydrogen ions by metal ions may usually be expected to proceed until equilibrium is established, which in the case of a divalent metal can be written

$$\mathrm{M} + 2\mathrm{H}^{\cdot} \rightleftharpoons \mathrm{H}_2 + \mathrm{M}^{\cdot\cdot}$$

This will occur when the concentration of $\mathrm{M}^{\cdot\cdot}$ ions and of H_2 molecules has become such as to make the potential $\mathrm{M} \mid \mathrm{M}^{\cdot\cdot}$ equal to the potential $\mathrm{H}_2 \mid \mathrm{H}^{\cdot}$ at the metallic surface. The necessary concentration of hydrogen in the liquid involves a certain pressure of hydrogen in the gas space above the liquid. In the case of the nobler metals the pressure involved is low, and equilibrium being soon established, all reaction ceases. But for the baser metals, equilibrium will only be reached when the pressure has become high (sometimes "astronomically" high). If the walls cannot stand this pressure, or if the vessel is open to the air, equilibrium will be impossible, and evolution of hydrogen will continue (rapidly in bubbles from the baser metals, or perhaps by slow diffusion through the liquid to the gas space from the intermediate metals).

In this corrosion process, the reactions are

$$\mathrm{M} = \mathrm{M}^{\cdot\cdot} + 2e$$

at the anode, and

$$2\mathrm{H}^{\cdot} + 2e = \mathrm{H}_2$$

at the cathode.

In general, the cathodic reaction will take place at any points o especially low overpotential, where molecular hydrogen can be formec most readily (see p. xxxii). The cathodic and anodic reactions may sometimes occur at contiguous points (or even alternately at the same point) this presents a contrast to corrosion of the oxygen-absorption type, wher the anodes and cathodes are relatively large areas (the former bare anc the latter usually oxide-covered).

Noble Metals. In the case of the metals at the top of the Potentia Series, the formation of a very small concentration of cations will serv to bring about the equilibrium

$$\mathbf{M + 2H^{\cdot} \rightleftharpoons H_2 + M^{\cdot\cdot}}$$

and the passage of metal into liquid will cease long before the hydroger concentration has approached the saturation value corresponding t 1 atmosphere. Thus metals such as gold, silver or copper do not commonl liberate hydrogen from acids. Apparent exceptions, however, occur i solutions which produce complex ions, so that the equilibrium is no reached. If copper is placed in boiling hydrochloric acid, the vapou contains a little hydrogen, chlorocuprous acid $HCuCl_2$ being formed, wit copper locked up mainly as the complex anion $[CuCl_2]'$. Potassiu cyanide solution, despite its alkaline reaction, attacks copper, forming complex cyanide with the anions $[Cu(CN)_2]'$. In dilute hydrochloric o sulphuric acid, copper is only attacked if air or an oxidizing agent i present ;* sulphuric acid containing potassium chlorate or permanganat produces relatively rapid attack.

Intermediate Metals. Metals like tin and lead, which stand belo hydrogen in Table I, might be expected to react freely with dilute hydrochloric acid in the absence of oxygen, liberating hydrogen. Actually however, the hydrogen overpotential of these metals is high (Table IV p. xxxii), and a very small cathodic current density would suffice to depres the potential of hydrogen evolution to the potential provided by tin o lead. Thus, in absence of air, corrosion is slow in dilute hydrochlori acid ; hydrogen evolution can be increased by contact with platinu black, which provides a cathodic surface of low overpotential. Toward sulphuric acid, lead is immune, owing to the sparing solubility of lea sulphate (in hot concentrated acid, the film sometimes breaks down) In hot concentrated hydrochloric acid, lead suffers appreciable corrosion still quicker is the attack by hydrobromic acid, which can be obtaine at high concentrations (14N), and builds complex anions containing lead

Iron. The first metal in the Potential Series to expel hydroge freely is iron. Its normal potential stands well to the negative side o that of hydrogen, whilst the overpotential of hydrogen evolution on a iron cathode is fairly low ; thus, although the overpotential attendin he anodic dissolution is appreciable, the working E.M.F. of the cell

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* A specimen of copper, partly plated with platinum and sealed in 1934 in a tube containing N/2 sulphuric acid under anaerobic conditions, was kindly presented to the autho by Prof. O. P. Watts of Wisconsin University. After eleven years, there is still no sign of attack and the liquid remains colourless.

Iron | Acid | Hydrogen

s sufficient to cause a lively effervescence. The attack is accelerated if trace of platinum salt is added to the acid, which deposits platinum on he metal and thus provides a cathode of still lower overpotential. oreign particles in the iron can act in the same way, e.g. graphite ; grey ast iron is attacked by dilute sulphuric or hydrochloric acid much more uickly than relatively pure iron, and here the addition of platinum salt auses practically no further acceleration, as noted by Richardson.[125] ead mild steels containing most of the cementite in *massive* form were ound by Hoar and Havenhand [81] to be attacked somewhat more quickly *ceteris paribus*) than those where the cementite was more dispersed. he massive cementite probably provides cathodic particles from which ydrogen can readily be evolved ; finely dispersed cementite has no such ffect, possibly because the very small particles are quickly undermined nd carried away by the hydrogen bubbles. There are, however, more mportant causes for the variation in the behaviour of different steels. ne factor favouring rapid corrosion is the presence of sulphur, which n certain forms catalyses the (otherwise sluggish) anodic reaction. ulphur present as iron or manganese sulphide is dissolved by the acid, ielding hydrogen sulphide, the real catalyst. If sufficient copper is resent in the steel, this appears to "fix" the sulphur in some way, so hat the attack on the metal is retarded.* Thus Hoar and Havenhand ound that if the ratio of copper to sulphur exceeded 1·38, the attack by itric acid became slower. Tin salts added to the solution produced the same effect, precipitating the hydrogen sulphide as stable tin sulphide, and diminishing the rate of attack on the steel.

The presence of copper (up to about 0·3%) in structural steel increases ts resistance towards the acid rain-water and condensed moisture typical of industrial districts (see p. 84) ; the life of plates may be considerably lengthened by such additions, as shown by the extensive observations of Hudson.[88] It is possible that the peculiar behaviour of British wrought iron, which contains slag arranged as strings or layers, depends on similar principles. Most of the sulphide present is likely to be found in these strings or layers of slag, and if the cut ends of plates or bars are immersed in acid, the attack penetrates rapidly along the slag layers, producing a curious "wooden structure". On the other hand, the portions between the slag strings or layers will be relatively pure iron, and attack starting from the face of a plate is found to develop and progress more slowly than on steel ; even when it ultimately reaches and taps a slag string or layer, there is a general tendency for the attack to be diverted sideways. Thus attack on wrought iron (of the slag-containing variety) is often found to be faster in some directions and slower in others than the attack on slag-free iron. The practical importance of this is discussed on p. 85.

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* Opinion differs as to whether the sulphide is present in the steel as stable copper sulphide, or whether the hydrogen sulphide formed by attack on iron or manganese sulphide is precipitated by the copper salts which will have appeared in the liquid.

Experiments by the author [39] (not quite correctly interpreted in th original paper) showed that acid acting on the *faces* of plates (withou access to the edges) at first attacked wrought iron more slowly than attacked steel; when it reached the susceptible layers, the attack becam faster on iron than on steel, but was deflected sideways.

Zinc. Zinc stands far below hydrogen in the Potential Series, an if brought into contact with platinum below dilute acid will pass readil into solution, hydrogen being eliminated from the platinum. In absen of such contact, the high hydrogen overpotential of zinc makes the attac on *pure* zinc slow; commercial zinc is also attacked slowly at first, bu as impurities (mainly cadmium, lead and often iron) pass into solutio and are reprecipitated as a black metallic sponge, the corrosion an evolution of hydrogen are speeded up. This black sponge presents a larg surface area and acts as an effective cathode, even if the constituent meta are such as would display high overpotentials in the massive state; the black sponge is brushed away, the evolution of gas slows down. Th author [34] has detected currents flowing between the zinc as anode an the sponge as cathode. The period of slow dissolution, which elapse before the attack becomes rapid, is called the *Induction Period.*

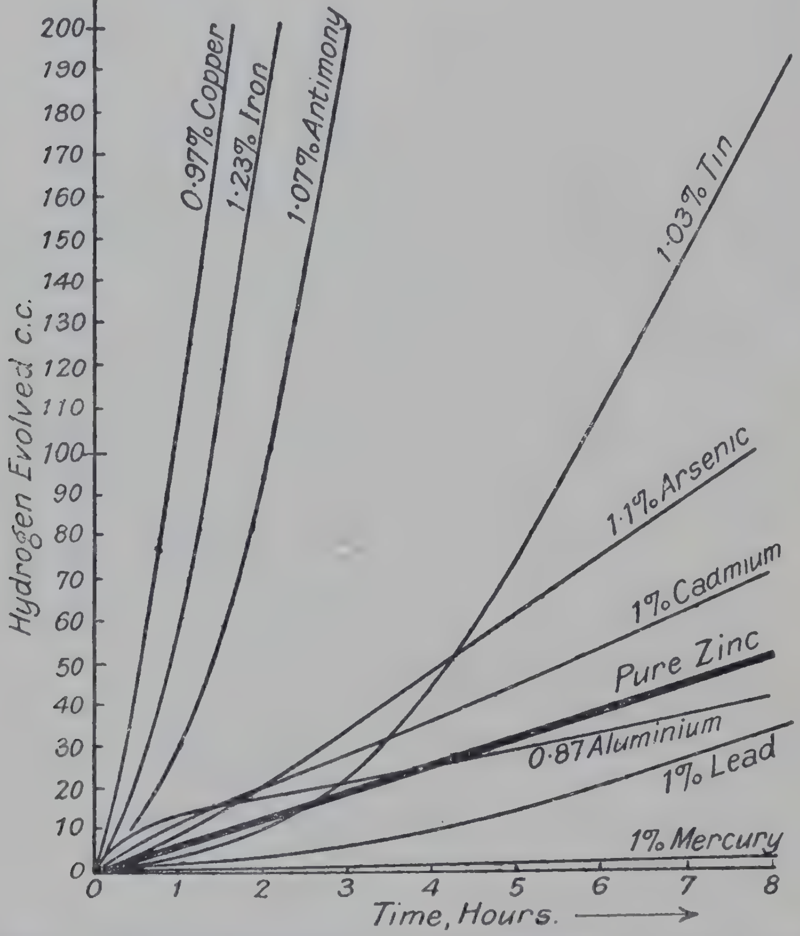

Fig. 34.—Effect of Minor Constituents on the Corrosion of Zinc by N/2 Sulphur Acid (R. Vondráček and J. Izák-Križko).

Naturally, those minor constituents are most effective which have low verpotentials. The curves of Vondráček and Izák-Križko [158] (Fig. 34) how that copper, iron and antimony cause most acceleration, the reaction ate increasing with time, whereas on relatively pure zinc the rate remains nchanged. Only reprecipitated impurities work in this way; tin in olid solution at first retards the attack, but, after it has begun to dissolve n the acid and has been redeposited in metallic form, the reaction rate ises above that of unalloyed zinc. Mercury greatly retards attack, aising the overpotential.

The attack of acids on zinc is greatly accelerated by the presence of xidizing agents such as potassium nitrate, nitrophenol or quinone. King and Braverman [96] have studied the action of hydrochloric or acetic cid containing potassium nitrate on rotating specimens, and find that pectroscopically pure zinc is then corroded almost as fast as “ordinary” inc, and that the rate of attack is not very different from that on nagnesium, cadmium or even calcium carbonate. Evidently, the velocity s determined mainly by the rate of replenishment of the acid used up in he reaction, and is largely independent of the chemical or electrochemical eactions proceeding at the surface.

Unlike iron, zinc evolves hydrogen from sodium hydroxide solution, orming “zincates” such as Na_2ZnO_2; despite the low hydrogen ion oncentration (which will depress the cathode potential), the fact that inc enters solution as complex anions $[ZnO_2]''$ or $[HZnO_2]'$, depresses he anode potential, and consequently a considerable E.M.F. remains to rive the reaction.

Aluminium. As explained on p. 42, sesquioxides are only very lowly dissolved through direct attack by acids. The “reductive disolution” which causes such a rapid destruction of ferric oxide films annot affect alumina films, since aluminium exists in one valency-state nly. Consequently aluminium, introduced into acid after air-exposure, xhibits a Period of Induction, which (in contrast to that met with on zinc) is due to the slow dissolution of alumina. On very pure aluminium the induction period may be measured in days; on the impure metal, t is much shorter, possibly because the sites of impurities constitute iscontinuities in the film. Moreover, impurities in solid solution in lumina may increase its electrical conductivity (p. 21), so that the film an function as a cathode towards the metal exposed at gaps more fficiently than the pure oxide formed on high-grade metal; pure alumina s too poor a conductor to act as cathode. One author has pictured oth the anodic and cathodic actions taking place at pores in the skin; ores filled with acid provide anodes, whilst those containing residual netallic impurities furnish cathodes. If pure aluminium is etched in oncentrated hydrochloric acid and then placed in more dilute acid, there s no period of induction, the film having been destroyed by the stronger cid.[18a]

Aluminium is attacked by caustic alkali without the induction period ound in acids, although the final attack is slower; alkalis seem to destroy

the protective alumina film very quickly, possibly because they ar
positively adsorbed.

Magnesium and Alkali Metals. The metals standing belov
aluminium in the Potential Series can evolve hydrogen even from neutra
liquids (magnesium from chloride solutions ; sodium and potassium fror
pure water). Naturally they react violently with acids. The attac
upon magnesium by hydrochloric and acetic acids was found by James[9]
to have a very low temperature coefficient, which is often regarded a
evidence that the velocity is controlled by the rate of replenishment c
reagent ; but James found his measurements to be independent of th
velocity of agitation, and considers that they really represent the velocit
of the reactions involved. A paper by Coates[21] on the electrochemistr
of acid attack on magnesium deserves study.

Attack by Nitric Acid

Base Metals. Although free hydrogen appears when *very dilu*
nitric acid acts on magnesium, the majority of base metals, on dissolvin
as nitrates, yield (in lieu of free hydrogen) hydrogen-rich compounc
formed by interaction between cathodically discharged hydrogen ior
and the nitric acid. These include ammonia (NH_3) and hydroxylamir
(NH_2OH), both present as nitrates, along with nitrogen (possibly produce
by decomposition of ammonium nitrite) and nitrous oxide (N_2O, possibl
produced from ammonium nitrate).

Noble Metals. In the corrosion of noble metals, the reduction c
nitric acid does not proceed so far. The anodic reaction (for a divaler
metal) may as usual be written

$$M = M^{\cdot\cdot} + 2e$$

but there is less agreement about the cathodic reaction. The followir
line of argument has been put forward by the author.[47]

The complicated equations published in textbooks must really tal
place in steps, and it seems logical that the cathodic reduction of nitr
acid should come about in simple stages thus :—

$$\begin{array}{lllll} (1) & HNO_3 + & H^{\cdot} + e = & NO_2 & + H_2O \\ (2) & NO_2 \quad + & H^{\cdot} + e = & HNO_2 & \\ (3) & HNO_2 + & H^{\cdot} + e = & NO & + H_2O \end{array}$$

each of which might also occur in the ionic form :

$$\begin{array}{lllll} (1a) & NO_3' & + 2H^{\cdot} + e = & NO_2 & + H_2O \\ (2a) & NO_2 & + e \qquad\quad = & NO_2' & \\ (3a) & NO_2' & + 2H^{\cdot} + e = & NO & + H_2O \end{array}$$

Of these six equations, ($2a$) involves only two particles (including tl
electron), and may be regarded as taking place more easier and frequent
than the others, which involve the meeting of three or four particles.
soon as a trace of NO_2 has been formed by (1) or ($1a$), it will quickly
reduced to $(NO_2)'$ by ($2a$), which will combine with hydrogen ions to gi
nitrous acid (HNO_2). This can readily react with nitric acid to regenera
twice the original quantity of NO_2 by the reaction

$$(4) \quad HNO_2 + HNO_3 = 2NO_2 + H_2O$$

which also involves only two particles and is therefore likely to occur easily. The $2NO_2$ will then rapidly be reduced by (2*a*) and rapidly oxidized by (4), yielding $4NO_2$, and so on. *At each cycle,* the quantity of the NO_2 (and HNO_2) involved will be *doubled,* and the reaction, which at the start involves only a few molecules, will soon become violent, involving large numbers of molecules, provided that the NO_2 (and HNO_2) remain on the spot. The increasing violence of this "autocatalytic" reaction will be obtained at crevices where one piece of metal rests on another, or at the cranny formed where the metal rests against glass. At such points, the products will not easily be dispersed, and the action will increase in violence (and with it the anodic attack on the metal, which must keep pace with the cathodic reactions), until the loss of HNO_2 through other reactions exactly balances the increase due to the cycle constituted by (2*a*) and (4).

One way in which HNO_2 can be destroyed is through reduction to nitric oxide (NO), by (3) or (3*a*). In the steady state when the total HNO_2 ceases to increase, the destruction of one molecule by (3)

$$HNO_2 + H^{\cdot} + e = NO + H_2O$$

must balance the *net* production of one molecule by (4) and (2*a*)

$$HNO_2 + HNO_3 = 2NO_2 + H_2O$$
$$2NO_2 + 2H^{\cdot} + 2e = 2HNO_2$$

In the steady state, the total change is obtained by adding these three equations, giving

$$HNO_3 + 3H^{\cdot} + 3e = NO + 2H_2O$$

Alternatively, especially if the volume of liquid is small, so that the reaction raises the temperature, nitrous acid may be destroyed by decomposition to NO and NO_2, which will then regenerate *half* the original quantity of HNO_2. Thus the *net* loss of one molecule by the cycle

$$2HNO_2 = NO + NO_2 + H_2O$$
$$NO_2 + H^{\cdot} + e = HNO_2$$

must balance the *net* gain of one molecule by the cycle

$$HNO_2 + HNO_3 = 2NO_2 + H_2O$$
$$2NO_2 + 2H^{\cdot} + 2e = 2HNO_2$$

Adding these four equations, we *again* arrive at

$$HNO_3 + 3H^{\cdot} + 3e = NO + 2H_2O$$

Thus the same result is obtained whether HNO_2 is lost by reduction, decomposition or both. This, the final sum of the reactions at the cathode in the steady state, must balance the electrical transfer of the anodic change

$$M = M^{\cdot\cdot} + 2e$$

To obtain electrical balance, it is necessary to double the cathodic equation, treble the anodic equation and add them together, so that the 6*e* transfer cancels out, giving

$$2HNO_3 + 6H^{\cdot} + 3M = 3M^{\cdot\cdot} + 2NO + 4H_2O$$

To preserve electric neutrality in the liquid, $6(NO_3{}')$ may be introduce on each side, so that the reaction can be written

$$2HNO_3 + 6H^{\cdot} + 6NO_3{}' + 3M = 3M^{\cdot\cdot} + 6NO_3{}' + 2NO + 4H_2O$$

or in non-ionic language

$$3M + 8HNO_3 = 3M(NO_3)_2 + 2NO + 4H_2O$$

—the equation usually printed in textbooks for the action of nitric aci on copper (where M = Cu).

It is easy to see why the action of nitric acid on such metals proceed most quickly at crevices. If the products of reaction are dispersed, th autocatalytic cycle will fail to develop the same violence, and for th same reason rapid stirring of the liquid is found to slow down the attac on copper or silver. A substance which breaks the autocatalytic cycl should have a similar effect; urea reacts with and destroys nitrous acid a key substance in the cycle, and accordingly it is found that the additio of urea to nitric acid greatly retards the corrosion of metals such as copper These autocatalytic characteristics are confined to the noble metals Hedges [73] states that stirring, which greatly retards the action of nitri acid on silver or copper, stimulates that on tin, zinc and magnesium.

Iron. Particularly interesting is the action of nitric acid on iron At low concentrations, the attack is most violent, and the behaviour i intermediate between that of the two classes of metals mentioned above The metal is attacked with greater violence in crevices than elsewhere but the products, besides nitrogen peroxide (NO_2) and nitric oxide (NO) include nitrous oxide (N_2O), nitrogen and ammonia. The behaviour i altered by cold-deformation which, by distorting the lattice and producin an unstable condition, makes the iron behave more like zinc. The proportion of $N_2 + NH_3$ to $NO + NO_2$ increases if the metal contains interna stresses, as shown by Whiteley and Hallimond; [161] by studying th composition of gases evolved when nitric acid acts on steel, they reache the conclusion that the iron in the pearlite areas of steel must be in a state of strain.

Nitric acid is, however, an oxidizing agent as well as an acid, an may produce a film of ferric oxide over the surface; if this once occurs corrosion is likely to cease, since sesquioxides only very slowly suffe direct dissolution in acids, and reductive dissolution (p. 84) is unlikely i a powerful oxidizing agent is present. Thus there is a contest between th acidic and oxidizing properties of the reagent. In dilute acid, corrosio proceeds violently; but concentrated acid, after a slight attack at th moment of introduction, renders iron passive and inert. At intermediat concentrations, behaviour depends on past history. Iron which has firs been dipped in concentrated acid can withstand introduction into weake acid capable of attacking iron which has not been pretreated in concentrated acid. In acid of borderline concentration, contact with zin (i.e. cathodic treatment) can cause passive iron to become active, wherea contact with platinum (anodic treatment) may render active iron passive There is no serious doubt that the passivity produced by the concentrate cid is due to an oxide film; Tronstad's optical studies [144] support that iew, and the thickness of the film has been estimated by Gulbransen,[69] ho measured the loss of weight when passive iron was ignited in hydrogen.

The passivity of iron in nitric acid is, however, very liable to break own, especially at a water-line. Hedges [73] found that, at certain conentrations, iron sheet was violently corroded if dropped flat on the urface, but remained uncorroded if plunged in edgewise. The author [36] ound that pure iron foil, dipped in concentrated nitric acid, withdrawn nd allowed to drain, suffered no attack at first; then suddenly a violent eaction would set in, usually at the top of the wetted area, and travel apidly downwards, until the whole surface was evolving bubbles. Apart rom the usual factors which cause protective films to fail at a water-line p. 135), there is here a special mechanism involved. When once attack as set in at a point from which oxides of nitrogen can escape, the ratio N_2O_5:H_2O falls, which must favour corrosion as opposed to passivity. Now an escape of gas is easiest at a water-line, and it is here that violent eaction so often sets in.

In another respect, the attack of nitric acid on iron differs from that on other metals. Any nitric oxide (NO) formed by reduction of nitrous acid, instead of escaping from the system, can be retained by combination with ferrous salts present, forming brown nitroso-compounds, such as $Fe(NO_3)_2.NO$, and remains available to enter an autocatalytic cycle. The brown coloration often seen on iron during experiments involving nitric acid is due to such compounds.

Choice of Materials for Chemical Works

Resistance to Acids. In choosing materials to withstand acids or alkalis, a metal can sometimes be selected which forms a sparingly soluble compound with the principal anion. Thus lead is often used to withstand sulphuric acid, silver to resist hydrochloric acid, whilst magnesium (which reacts violently with most acids) has been recommended for handling hydrofluoric acid (a reagent which attacks many otherwise resistant materials); the behaviour of the three metals is probably connected with the low solubilities of lead sulphate, silver chloride and magnesium fluoride.

In cases where a metal forms oxides which possess acidic but no marked basic properties, the action of acids is likely to produce an oxide film rather than a soluble salt, and good resistance may be expected. Thus tantalum, molybdenum and tungsten form well-defined tantalates, molybdates and tungstates, but the sulphates of these metals are unknown or unstable. Accordingly, all three metals offer considerable resistance to non-oxidizing acids; tantalum, for instance, has proved useful for handling hot hydrochloric acid. The manner in which molybdenum and tungsten withstand hot sulphuric and hydrochloric acids is shown in Table IX, which also brings out the resistance of certain nickel alloys containing those elements. Among American alloys with nickel and molybdenum as main constituents, Hastelloy A with 58% Ni, 20%

20% Fe and 2% Mn resists hydrochloric acid in absence of oxygen ; oxygen or chlorine is to be present, Hastelloy C with 58% Ni, 17% M 6% Fe, 14% Cr and 5% W has been recommended.

Non-metals, the oxides of which possess no basic properties, naturall suggest themselves as acid-resistant materials, but their physical properti are generally unsuitable. However, by introducing silicon into cast iro alloys are obtained which, although brittle, can be made into acid-pro castings suitable for use at chemical works. For handling sulphuric aci iron containing about 14·2% silicon is generally suitable.

TABLE IX

Corrosion of Metals and Alloys by Hot Acids (W. Rohn)
(expressed as grams per square decimetre in 1 hour)

	10% HNO_2	10% H_2SO_4	10% HCl	10% HAc	10% H_3PO_4
Iron (annealed)	36·7	15·6	21·0	0·76	12·3
Nickel (annealed)	9·07	0·02	1·51	0·004	0·044
Chromium	nil	45	150	0·03	nil
Molybdenum (hot-rolled) .	1·8	0·0015	0·0015	0·003	0·009
Tungsten (hot-rolled) . . .	0·06	0·01	0·01	—	—
*Alloys (annealed) with—					
Fe 15, Ni 61, Cr 15, Mn 2, Mo 7%	nil	0·02	0·02	0·006	0·016
Fe 16, Ni 61, Cr 15, Mn 2, W 6%	0·01	0·02	0·18	0·002	0·03
Fe 20, Ni 64, Cr 15, Mn 1%	0·02	0·11	1·97	0·01	0·062

* These alloys are known as *Contracid B7M*, *Contracid B6W*, and *Chroman B* respectively

The high anodic overpotential of nickel (p. xxx) causes it to react mucl more slowly than its position in the Potential Series would seem to predict.* Some of the nickel alloys possess special value. One of these is *Mone Metal*, made by the reduction of a certain nickel-copper ore withou separation of the metal ; it usually contains about 67% Ni, 30% Cu, witl small (but carefully controlled) amounts of other elements, including Mn (about 1·25%), iron (about 1·25%) and still smaller quantities o carbon and silicon. It is used for acid-pumps, filters and the like Varieties containing aluminium are employed for battery terminals, and those with a higher silicon-content in places where wear or high-pressure steam will be encountered. Synthetic alloys can, of course, be made up to these compositions, but apparently they are only equal to the " natural " Monel if all the carbon is in solid solution ; graphite flakes promote attack. The corrosion of Monel Metal by acid, although very small under anaerobic conditions, increases steadily with oxygen-content.

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* The good resistance of nickel to some acids may also be attributed to the fact that nickel oxide-films are only slowly dissolved by acids—as has been proved by experiments on heat-tinted nickel. The reductive dissolution which destroys Fe_2O_3 films cannot operate on NiO. The acid-resistance of nickel may thus be compared to that of aluminium, which is invariably trivalent.

It might be expected that for handling concentrated nitric acid, nalloyed iron or steel, which usually becomes passive in that liquid, ight be used. However, although small pieces of iron can be kept in oncentrated nitric acid without attack, there is always a small chance of reakdown, and, with large areas, the probability of attack—especially at urface imperfections or in the event of scraping—becomes serious. Thus on or steel cannot generally be relied upon as a safe material for the oncentrated acid; if, for instance, accidental dilution occurred locally .g. from condensed moisture flowing down into the acid), attack might tart and spread. If, however, sulphuric acid (which depresses the ctivity of any water) is present mixed with the nitric acid, ordinary steel an generally be used in contact with the mixture, at least at high conentrations; it is advisable to keep the sulphur content of the steel low nd the carbon fairly high.

Sulphuric acid, without nitric, renders iron passive if sufficiently conentrated, being itself an oxidizing agent. Iron and steel vessels are requently used for handling the acid above 70%; there is a danger, owever, of absorption of moisture from the air, and if the concentration alls below 60% attack may become serious.

In the case of certain other metals, the oxidizing character of concenrated sulphuric acid leads to attack rather than to passivity. Copper, hich is only attacked by the dilute acid in presence of oxygen, reacts eadily with the hot concentrated acid. The reaction clearly takes place n steps, but the final result is usually written

$$Cu + 2H_2SO_4 = CuSO_4 + SO_2 + 2H_2O$$

The resistance of copper to many reagents is increased by the introuction of silicon or aluminium; *Everdur*, containing 3% Si and 1% Mn more of each for casting), was developed largely to resist hydrochloric cid.

Stainless Steels.[111] Since the destruction by acid of ferric oxide lms is essentially a reductive dissolution, it would seem logical to tabilize the films by introducing an element in which the divalent ondition is relatively unstable. Chromium is such an element, and indeed nalloyed chromium is remarkably resistant to 10% nitric acid, which apidly attacks iron (see Table IX, p. 64). If introduced into steel, it onfers similar immunity to nitric acid; the best results are obtained rom an austenitic steel, consisting of a single phase, since phase-oundaries are liable to be points of weakness. A suitable composition ontains 18% of chromium along with 8% nickel, added to stabilize the ustenitic condition. This “18/8 alloy” (the main use of which depends on its resistance to *atmospheric* attack) is sold under various trade names uch as “Staybrite” and “Alleghany Metal”; “Anka” is an austenitic alloy of the same type. In order to obtain the one-phase state, the naterial is heated at about 1100° C. and then quenched.

The austenitic stainless steels show considerable resistance to sulphuric acid if oxygen is present; but the removal of the last trace of oxygen may permit serious attack. Other substances can play a useful part preserving the passive state, such as traces of copper sulphate (oft derived accidentally from bronze pumps), or even ferric sulphate. confer resistance against dilute sulphuric and hydrochloric acids unc anaerobic conditions, molybdenum is added to the metallic phase; British alloy known as BB4K contains 3 to 4% molybdenum in additi to chromium and nickel in the usual amounts (e.g. 18/8). Such moly denum alloys are also useful for resisting sulphurous acid—a reage important in the paper and textile industries. Austenitic alloys containi the non-metal, silicon, serve a similar purpose. The role of molybdenu and silicon in conferring acid-resistance was discussed on pp. 63, 64.

The resistance of stainless steels is diminished by surface defects a particularly by foreign matter rolled into the material; the atmosphe of the rolling mill must be kept free from all suspended particl Similarly mill-scale rolled into the surface may cause a breakdown passivity, and attention must be given to pickling. This is sometim carried out in a single hot bath containing hydrochloric acid, nitric ac and a pickling inhibitor. An alternative process requires two baths; t articles are first treated in a solution containing sulphuric and hydr chloric acids at 60° C., and then, after rinsing, in a mixture containi nitric and hydrofluoric acids at 30–40° C., no inhibitor being used either bath.

The troubles sometimes caused around welds in austenitic stainl steel are discussed on p. 113.

Aluminium. Whilst in chromium the divalent condition is unstab in aluminium it is absent altogether, which would suggest this trivale metal as a material suitable to resist oxidizing acids. Unfortunate aluminium occupies a low place in the Potential Series, and the essentia reactive character of the metal itself must be set against the protecti character of the alumina film. For handling nitric acid of concentrati above about 96%, aluminium is used with satisfaction. Below th concentration, the attack becomes rather too fast to make the emplo ment of aluminium a practical proposition, although even at the concentr tion where the attack is most rapid (about 30% nitric acid), the action very sluggish compared to that on iron. The velocity varies greatly wi the minor constituents present in each material, but it may be rough true to say that the attack on aluminium in a year is equal to that mild steel in two hours. The attack on aluminium at any given conce tration is greatly stimulated by the presence of traces of chlorides.

Aluminium is also much used for resisting organic acids. Seligm and Williams,[130] studying the effect of hot organic acids, report sor curious features. Dilute (1%) acetic acid attacks aluminium somewh readily, but the corrosion rate diminishes as concentration increase 99% acid is almost without action, but the removal of the last 0·05% water increases the attack one hundred times. Rather similar resul have been obtained with propionic and butyric acids, phenol and wi ethyl, butyl and amyl alcohols. The absolutely anhydrous substanc ttack the metal, but a mere trace of water serves to protect, evidently ecause aluminium can displace hydrogen from water, forming a film of lumina. The fact that alumina should be formed in an acid electrolyte as aroused surprise, in view of the low $(\mathrm{OH})'$ concentration, but it is eally no more surprising than the cathodic evolution of hydrogen from n alkaline solution. In any case, it is a demonstrated fact (p. 150) that he anodic treatment of aluminium in sulphuric acid under an external E.M.F. gives an oxide film of considerable thickness.

The film-forming power of small amounts of water is of great practical importance. For making acetic, propionic or butyric acids of high concentration, aluminium plant should enjoy a reasonable life, provided that there is no risk of complete dehydration—or of undue dilution.

The resistance of aluminium to acids depends largely on the purity of the metal and the exclusion of chlorides and metallic salts from the acid. Great care must be taken not to introduce impurities into originally pure aluminium either from tools, or by the rolling in of metallic particles which have settled on the surface. Even emery particles embedded in an abraded surface can increase the rate of attack, whilst inclusions near the surface—due to inverse segregation—can be responsible for pitting; sometimes the casting skin, which contains such impurities, is removed before rolling. Porosity, due to evolution of hydrogen in the molten aluminium before casting, may also cause attack; hydrogen can originate from corroded scrap aluminium included in the charge, being formed when the moisture in the corrosion product acts on the hot metal; any hydrogen present should be removed by washing the molten metal with chlorine and/or nitrogen before casting.

Welding may also be the cause of corrosion trouble on aluminium. When making welds in aluminium of commercial purity, there is some benefit in using filler rods of a still higher degree of purity. In making storage tanks for nitric acid, the welds should be hammered, annealed and thoroughly washed before use, especially if chlorides have been present in the flux used. Most fluxes contain alkali fluorides, often with chlorides to reduce the melting point, but even with potassium bisulphate flux, washing is important. It should be remembered that particles of flux entrapped in the molten metal may remain after washing, and constitute sources of weakness, besides setting up corrosion. Closed blow-holes within welds on aluminium—whether due to hydrogen or other cause—are rapidly picked out by nitric acid; similar holes in stainless steel welds may never come to light in service.

Metals to withstand Alkali. The solubility of metallic oxides in alkali is much more widespread than is generally supposed. Zinc, aluminium, lead, tin and even copper are all attacked by sodium hydroxide solution, at least if oxygen is present. The metals most resistant to alkali are nickel, silver and magnesium. Nickel is largely employed in reactions involving hot alkali, whilst silver is sometimes used in contact with caustic soda up to 80%; the resistance of silver deteriorates if nitrates are present.

Iron becomes passive in dilute sodium hydroxide, but in concentrat alkali, at least at high temperatures, it can pass into solution as sodiu *ferroate*, Na_2FeO_2, (“ hypoferrite ” would be a more logical name)— compound of divalent iron. This change, important in connection wit “ caustic cracking ”, is discussed on p. 110.

Graphical Construction for Corrosion Velocity *

Non-Oxidizing Acids. The reason why iron placed in dilute su phuric acid suffers steady attack, with expulsion of hydrogen, is simpl because, under the concentration conditions set up at the metallic surfac the P.D. of $H \mid H^{\cdot}$ lies on the positive side of $Fe \mid Fe^{\cdot\cdot}$, so that there is a E.M.F. (represented by the distance between these two P.D.s) to maintai current flow, and thus corrosion. But fortunately the current flowing far less than the value obtained on dividing the unpolarized value of th E.M.F. by the resistance of the circuit. When current flows betwee the anode and cathode both potentials (A and C) are shifted so as t approach one another, as show in Fig. 35. However low th resistance, the current flowin could never exceed the valu (representing the abscissa of th intersection point, *P*) which woul render the acting E.M.F. vanishingly small. In acid corrosio (where the solutions are usuall good conductors whilst the anode and cathodes are generally clos together), no great error is involved in the assumption that th intersection point does represen the current flowing ; if the current is I amperes, the corrosio rate will be I/F gram-equivalents per second, where F is Faraday' number (98,487).

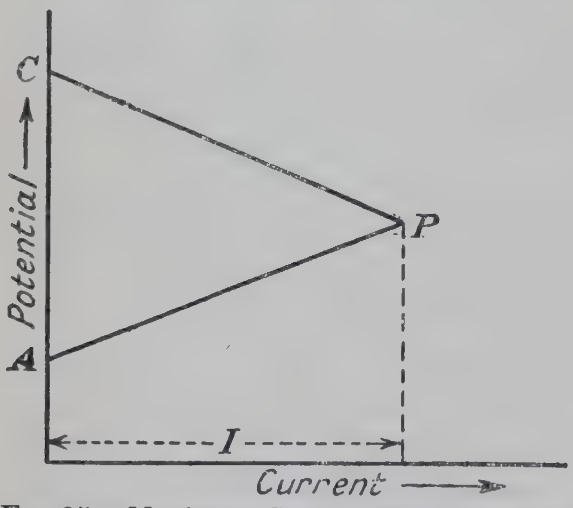

Fig. 35.—Maximum Current obtainable from Low-Resistance Corrosion Cell.

The slope of the hydrogen curve will depend on overpotential, an will be steeper for zinc, which has a high overpotential, than for iro (Fig. 36). Thus, notwithstanding the fact that zinc (the more reactiv metal) will have an anodic curve lower than iron, it will corrode (in th absence of contact material) more slowly than iron, the rates bein indicated by the abscissæ of P and Q respectively. If a little platinu salt is added, the black platinum deposited will have an overpotential lowe than that of either metal, and the corrosion rate of iron will be increase to a value represented by the abscissa of R.

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* For simplicity, all Polarization Curves in this section are represented by *Straight Lines* although the experimental curves in some cases depart from straightness. To assist understanding, the graphical construction for *Neutral Salt Solutions* (which strictly should hav received study in Chapter II) is considered after the (simpler) cases of *Acid Attack*.

In steel, as explained on p. 57, the presence of massive cementite facilitates the cathodic reaction, probably by providing points of low overpotential; thus (Fig. 37) the cathodic curve in presence of massive cementite is less steep than in its absence (CP_1 instead of CP_2) and the corrosion rate becomes faster (P_1 instead of P_2). In the absence of massive cementite, hydrogen sulphide (produced by the attack on sulphide inclusions) will reduce the "stickiness" of the anodic reaction, rendering the anodic curve less steep and increasing the corrosion rate (P_4 instead of P_2). In a number of steels all free from massive cementite but differing in the content of sulphur and copper (which serves to render sulphur unavailable, fixing it in stable form), the cathodic curves will be CP_4 in all cases, although the anodic curves (AP_2, AP_3, AP_4) will differ. The potentials of the corroding steels will be given by the ordinates of the various inter-

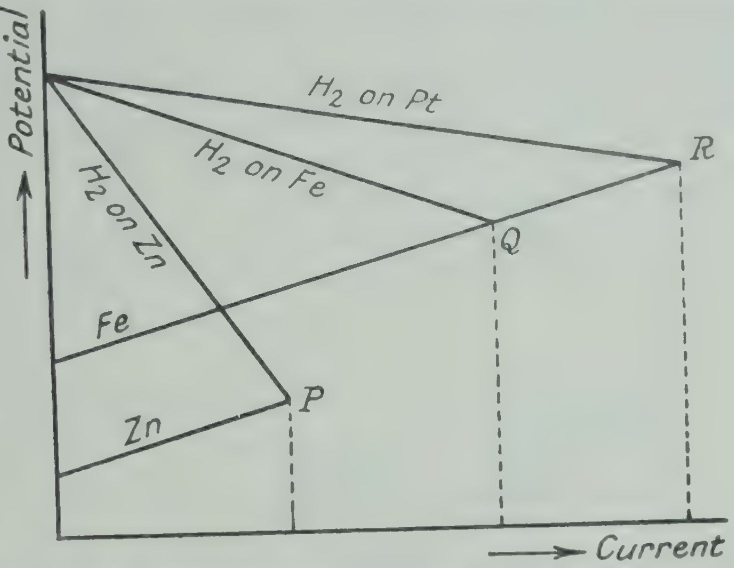

Potential
H2 on Pt
H2 on Fe
H2 on Zn
R
Q
Fe
P
Zn
Current

FIG. 36.—The Action of Non-Oxidizing Acids on Zinc and Iron.

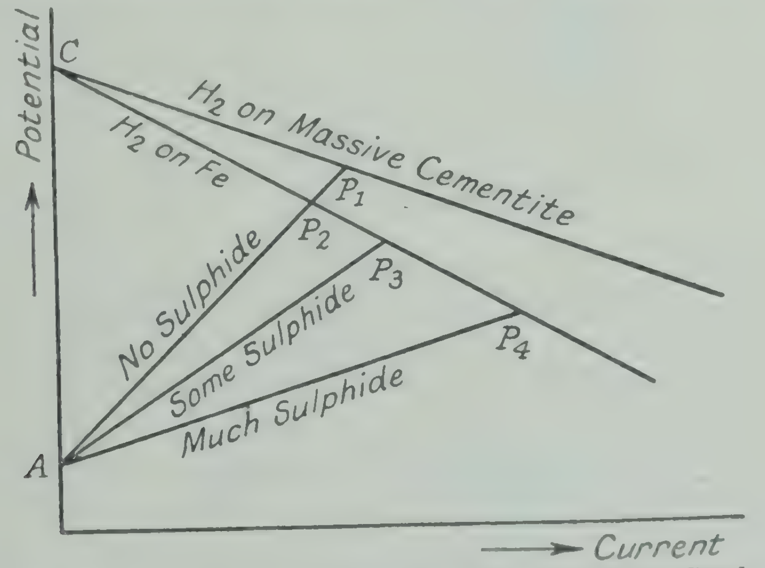

Potential
C
H2 on Massive Cementite
H2 on Fe
P1
P2
P3
P4
No Sulphide
Some Sulphide
Much Sulphide
A
Current

FIG. 37.—The Action of Non-Oxidizing Acids on Steel.

section points, and the currents flowing by the abscissæ ; since the inte section points must all lie on the curve CP_4, it follows that this single curv represents the relation between corrosion potential and current (and thu the relation between potential and corrosion velocity), as shown by Hoa and Havenhand.[81] The fact that there is here a definite relation betwee corrosion potential and corrosion velocity is of practical importance, sinc it is far quicker to measure a potential than a corrosion velocity.

Copper, in the absence of complex-forming bodies, exhibits a positiv potential, far above that of hydrogen-evolution (Fig. 38), and clearl there will be no E.M.F. available to provide for its dissolution in oxygen free acid. If oxygen is present, the cathodic curve is shifted upwards t a new level representing the conversion of O_2 to $(OH)'$, instead of th

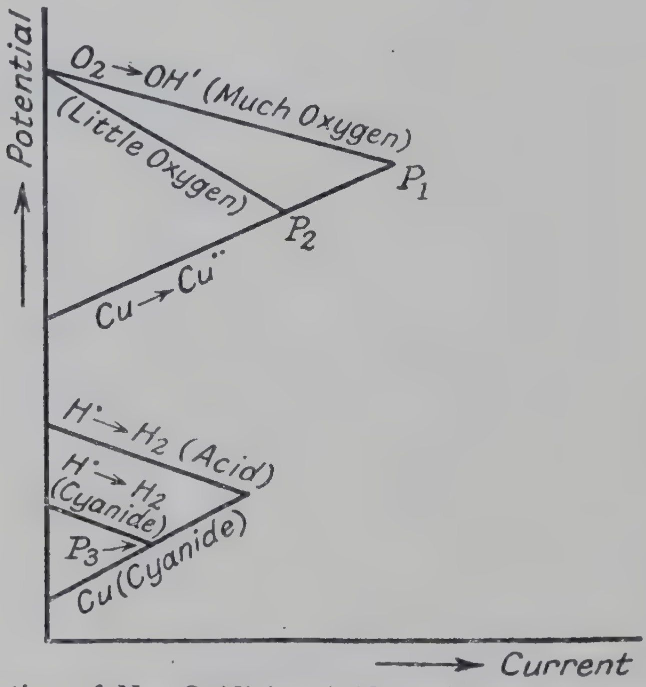


FIG. 38.—The Action of Non-Oxidizing Acids and Cyanide Solutions on Copper.

conversion of $H^{\cdot}$ to H_2. In this way corrosion becomes possible. Th cathodic reaction will polarize less if oxygen is replenished freely than i it is supplied scantily, and the curve is less steep in the first case, causing more rapid corrosion (P_1 instead of P_2). If a potassium cyanide solution is used instead of acid, the formation of complex ions causes a depression of the copper potential, and, although the hydrogen curve is also depressed owing to the alkaline reaction, slow corrosion at a rate represented by P can occur in absence of oxygen.

Oxidizing Acids. If, in considering the corrosion of iron, nitric acid is substituted for sulphuric, the cathodic reaction, instead of being the evolution of hydrogen (curve CP_1, Fig. 39), will be the reduction of nitric acid to various products, which will take place at much higher potentials (curve $C'P_2$). Thus the corrosion will be much faster (P_2 instead of P_1), and will tend to become greater as the acid concentration increases (since this will render the cathodic curve less steep). If, however, passivity ets in, the anodic potential will suddenly shift from the negative value hown by AP_2 to a positive (noble) value indicated by $A'P_3$; thus the ate of corrosion will become very slow (as represented by P_3).

Salt Solutions in Presence of Oxygen. The graphical method

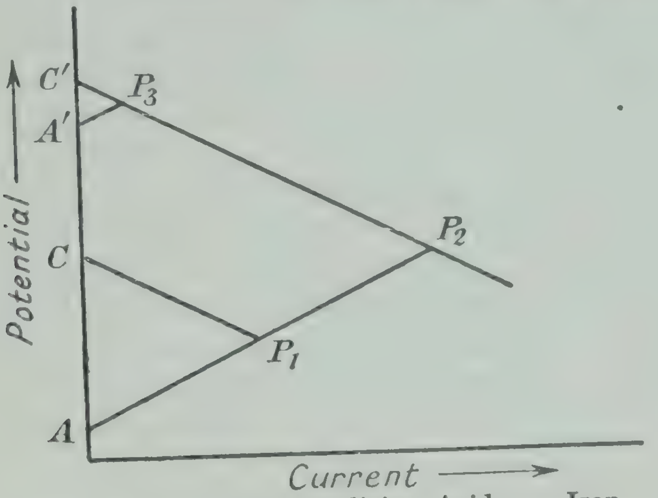


FIG. 39.—Action of Oxidizing Acids on Iron.

can be applied to corrosion by neutral solutions, but, except at high concentrations, the resistance must now be taken into account. In general, the current will be such a value (I) as will produce an intercept between the cathodic and anodic polarization curves equal to IR, where R is the resistance of the cell (Fig. 40).

If we consider a series of vertical iron specimens of the same shape

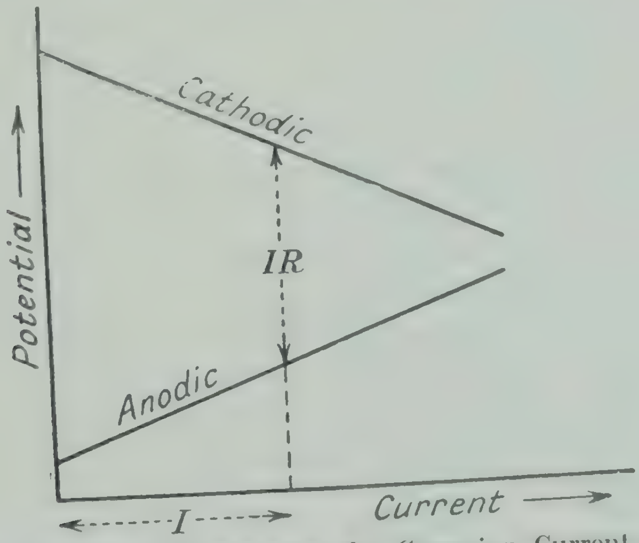
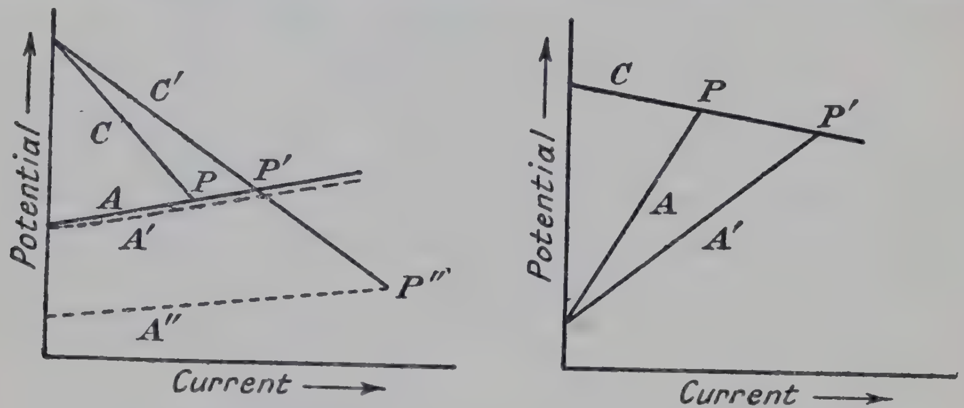


FIG. 40.—Graphical Construction for Corrosion Current obtainable where Resistance is appreciable (U. R. Evans).

partially immersed in salt solution of different concentrations the cathodic curve will of course represent the reduction of O_2 to OH' and the anodic curve the change from Fe to $Fe^{\cdot\cdot}$. At very low concentrations R will be high, and a large IR intercept being necessary, the corrosion rate will be small; but as the concentration increases, smaller intercepts will be needed, and the corrosion rate will increase towards that represented by the intersection point. When the intersection point is closel approached, further decreases of resistance will clearly have little effect since the rate of attack can never exceed that represented by the intersection point—however low the resistance may become. At first sigh it would seem that, with increasing concentration, the corrosion rat would asymptotically approach the value given by the intersection point However, at high concentrations, another factor comes in : the oxygen solubility of salt solutions falls off with the salt concentration, so that th cathodic curve (which depends on oxygen-supply) steepens, and th position of the intersection point itself shifts towards the left. Thus th corrosion velocity, after first increasing with concentration, will late start to diminish again. In the researches of Hoar and the author [52] o partly immersed specimens the maximum corrosion velocity was reache at concentrations between 0·3 and 0·6N, according to the variety of iro and salt employed. In the experiments of Bengough, Lee and Wormwell on fully immersed specimens, where the velocity was controlled essentiall



(I) Cathodic Control (II) Anodic Control

FIG. 41.—Cathodic and Anodic Control.

by oxygen-supply, resistance being unimportant, the maximum was placed at a very low concentration, and certainly from 0·01N upwards, the corrosion rate *declined* with increasing salt concentration.

Cathodic and Anodic Control. Let us consider, for simplicity, a case where the resistance is low, so that the intersection point defines the corrosion velocity. If the cathodic curve is much steeper than the anodic (Fig. 41 (I)) it is clear that an influence which stimulates the anodic reaction (say by halving the steepness of the anodic curve) will hardly move the intersection point, and thus will not appreciably alter the corrosion rate. But an influence stimulating the cathodic reaction (i.e. reducing the steepness of the cathodic curve) will greatly shift the intersection point and thus increase the corrosion velocity (e.g. from P to P′). This state of affairs, where the corrosion velocity is affected by happenings at the cathode but not appreciably by occurrences at the anode, is called *Cathodic Control.* An example is provided by the corrosion of iron in concentrated potassium chloride or sulphate, where, as just explained, the corrosion velocity is dependent mainly on the rate of supply of oxygen, the cathodic stimulant, whereas the nature of the anion hardly affects the rate directly, and any influence is indirect—due to changes in the oxygen-solubility.

If the anodic curve is much steeper than the cathodic, then factors stimulating the anodic reaction will greatly increase the corrosion rate, but those stimulating the cathodic reaction will hardly affect the corrosion velocity. This is called *Anodic Control* (Fig. 41 (II)), and examples are provided by the corrosion of aluminium in certain solutions containing chlorides and chromates. The anodic areas are here small defects in a protective film, and the introduction of small quantities of stimulating anions (such as chlorine ions) will greatly accelerate the velocity of corrosion, where cathodic stimulators (oxygen or oxidizing agents) will not increase the attack ; indeed, sometimes, by repairing the film, and thus reducing the anodic areas, they will retard it.

In practice, cases are common where the gradients of both curves are of the same order of magnitude. This is known as *Mixed Control.*

Potential Movement with Time on an Oxide-Covered Metal. Consider a specimen of metal covered with a nearly complete conducting oxide film (as a result of long exposure to air) plunged into a salt solution. Let the potential be measured just after immersion, and then again at suitable intervals. At first the current will be passing between the film as cathode and the metal exposed at occasional cracks in it as anodes. If the film is nearly complete, the resistance (R) will probably be somewhat high, and the current will be the value i just sufficient to produce an intercept iR (Fig. 42). The potential measured by a tubulus pressed against the surface will be represented by P.

Now if the solution is one which tends to repair the defects in the skin (i.e. to render the metal passive), the anodic area will become smaller and the anodic curve will steepen (from A to A′ ;) the resistance will rise (to R′) and since longer intercepts are needed, the measured potential must tend to rise also (e.g. to P′). But if the solution is an activating one, causing the damage to extend, the anodic curve will become less steep, the resistance will fall, the intercept will become smaller ; thus the potential will fall. Consequently, the direction of movement of the potential will indicate whether the liquid is tending to make the metal passive or active, whether it is stifling corrosion or promoting it. This is valuable information, and accordingly potential-time curves have been measured for many metals and alloys in many liquids. They do not, in general, provide any substitute for measurements of corrosion velocity.

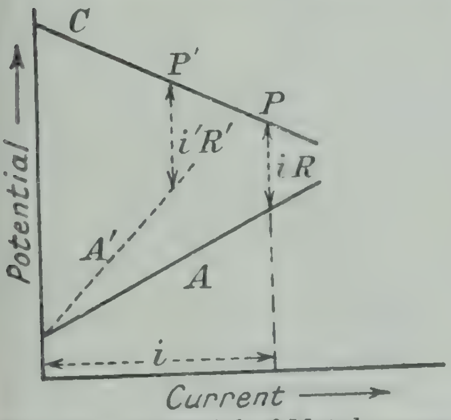


FIG. 42.—Potential of Metal covered with a Porous Film.

CHAPTER IV

INFLUENCE OF ENVIRONMENT

General

Contrast between Conditions of Atmospheric Exposure and Total Immersion. The examples of attack considered in Chapter II were largely taken from researches carried out, at Cambridge, on specimens *partially immersed* in salt solutions with an ample supply of oxygen to the upper part and a superabundance of water at the lower portion. In some respects, partial immersion constitutes a state of affairs intermediate between the conditions of *atmospheric exposure* studied by Vernon,[147] and the conditions of *total immersion* investigated by Bengough and his colleagues.[8] These two series of accurate research were started at the Royal School of Mines, South Kensington, and transferred later to the Chemical Research Laboratory, Teddington. In each type of corrosion, oxygen and an electrolyte usually play an important part; it is their relative supply which varies with the conditions.

Specimens freely exposed to the atmosphere will receive plenty of oxygen, but often very little moisture. In absence of electrolytes, a directly formed oxide film would stifle its own growth (p. 1). The presence of any electrolyte which can collect moisture and lead to a soluble corrosion product stimulates attack. Thus nickel remains bright in pure air, but when exposed indoors in moist air containing sulphur dioxide it becomes dull. Vernon[150] found that this "fogging" of nickel only takes place in air of R.H. (relative humidity) exceeding 70%; above that value, the invisible adsorbed film of sulphurous acid is oxidized, through the catalytic influence of the nickel, to sulphuric acid, which, being hygroscopic, collects water; consequently visible dew appears, even though the temperature is above dew-point. At first, the dew consists of sulphuric acid with dissolved nickel sulphate, and such a film can be wiped away with a cloth. Later, possibly during periods when the sulphur dioxide content of the air declines, solid basic sulphate appears in tenacious form, so that brightness can no longer be restored by wiping. In practice, fogging is generally prevented by covering the nickel with a thin overlay of chromium.

Similarly iron, which in pure dry air suffers no visible change, soon becomes rusty if exposed to salt spray. Here the primary corrosion products are probably soluble ferrous chloride and sodium hydroxide—both hygroscopic bodies—while in spray of marine origin, the magnesium chloride present is also hygroscopic; the surface will remain damp even though exposure to spray ceases, and rusting, once started, is likely to continue.

On the other hand, specimens of iron fully immersed in water or salt solution as in Bengough's experiments[8] will suffer attack at a rate largely dependent on the supply of oxygen to the metal. The addition to very pure water of small amounts of a salt (e.g. potassium chloride) will increase the rate of attack, but larger amounts of salt cause the corrosion velocity to decline again, because oxygen-solubility falls off as salt concentration rises (p. 72). If we disregard a small amount of corrosion connected with hydrogen-evolution, the attack can never exceed a limiting rate determined by the arrival of oxygen at the surface, although on highly resistant substances this rate may not be reached.

Clearly the corrosion velocity is subject to a different *controlling factor* in these two cases. In *atmospheric* attack, the main controlling factor is *moisture*; under conditions of *total immersion* it is *oxygen.*

Variation of Order of Merit with Conditions. The same substance may behave differently when brought into contact with a given liquid in two different ways. Zinc, placed in sodium chloride solution containing oxygen, is attacked more quickly than iron (other things being equal), largely because the E.M.F. of the cell Zinc | Oxygen exceeds that of the cell Iron | Oxygen. If the two metals are exposed to *fine* salt spray, the zinc is usually less attacked than the iron; here the soluble primary products (metallic chloride and sodium hydroxide) interact very close to the metal to give a largely adherent layer of hydroxide, which in the case of zinc has a partially protective character; the layer formed on iron gives less protection, probably because the ferrous hydroxide is converted to ferric hydroxide with a change of volume and interruption of continuity.

Even under fixed conditions of exposure, the order of merit of two or more substances will vary with the substances to which they are exposed. Magnesium is more rapidly attacked by sulphuric acid, but less rapidly by hydrofluoric acid, than is lead.

Tests. Clearly the idea, once widely held, that it should be possible, by means of a " standard corrosion test ", to establish an " order of merit " of materials which would be valid for all conditions, is wrong. The order of merit is different in different environments, and thus no one test can give the right results for all cases. Any test designed to decide the best material to withstand one particular set of conditions must be carried out in a form chosen to represent those conditions—perhaps intensified in order to give quick results, but free from any irrelevant influence.

In atmospheric exposure, behaviour varies according as the materials are washed by the rain or protected from it. For the latter conditions, Hudson[88] placed his specimens in Stevenson Screens—the open-work boxes used by meteorologists to accommodate their instruments. For exposure to weather, the frame shown in Fig. 43 has been used in the tests organized from Cambridge; it can be placed on any flat roof—provided that there is no unequal sheltering from rain, wind or sun—and the specimens, placed at 18° to the horizontal, do not screen one another. For complete immersion in the sea, specimens are often attached to rafts, whereas for intermittent immersion, they may be attached at half-tide level to a pier or other non-floating structure.

Many attempts have been made to simulate natural conditions in the laboratory, often in intensified form, so as to obtain an "accelerate corrosion test". At one time, it was thought that exposure in a bo filled with air containing fine particles of salt spray or acid spray shoul serve to assess the relative resistances of materials to sea air and town ai respectively. In one form of spray test, the specimens are kept wette continuously, and the changes which in natural exposure occur to th corrosion product whenever it dries up or reabsorbs water (changes whic affect protective properties) are left out of account. By applying th spray intermittently, with intervening periods of drying, an order of meri is obtained which accords better with that obtained on natural exposur to the weather. In modern testing, specimens are often attached to a endless belt-conveyor, so that they are alternately subjected to a spra and a drying lamp; sometimes a douche is incorporated in the cycle Vernon [152] has improved the spray test by using liquids containing substances which he had found to play a part in natural corrosion by polluted atmospheres; a solution containing sulphuric acid (N/500), sulphur dioxide (0·02% by volume), ammonium sulphate (N/50,000) and carbon dioxide (nearly to saturation) gave good agreement with the results of field tests, particularly bringing out the effect of copper in steel.

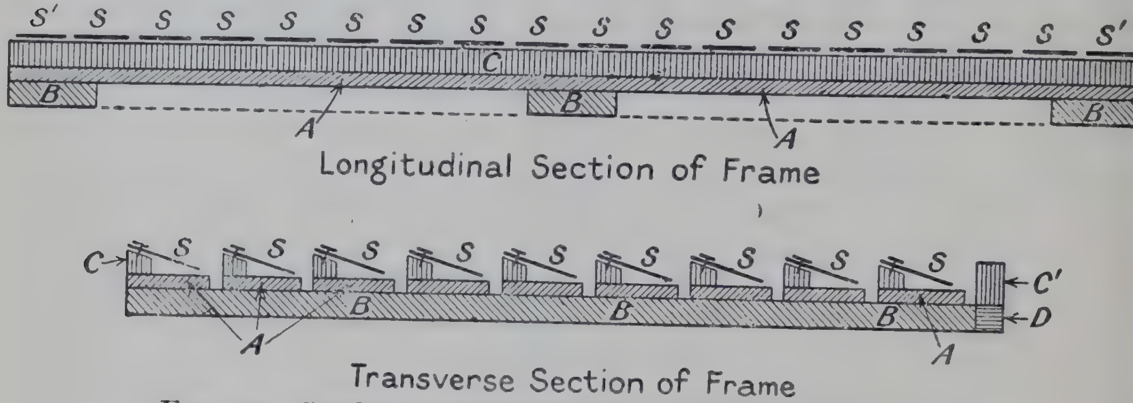


FIG. 43.—Cambridge Exposure Frame for Small Specimens.

S, steel specimens; *S′*, dummies; *A*, *B*, and *C*, wooden strips.

Laboratory testing apparatus is also available to provide, with or without agitation, total, partial or intermittent immersion in any liquid whose action on a series of metals is under investigation.

Criteria of Progress. As a measure of the corrosion which has occurred, the gain in weight of a specimen may be used where the corrosion product remains adherent, e.g. in high-temperature oxidation or atmospheric attack. If the product is soluble or loose, as often in immersed corrosion, the loss of weight is a better criterion; it must be determined after complete removal of the product, e.g. by acid containing enough inhibitor (p. 144) to prevent attack on the metal during the cleaning.

Alternatively, the amount of metal found in the corrosion product (whether dissolved, loose or adherent) may be estimated; where the amount is small, colorimetric methods are available, and photoelectric apparatus such as the "Spekker" makes possible accurate studies of the opening stages of attack.

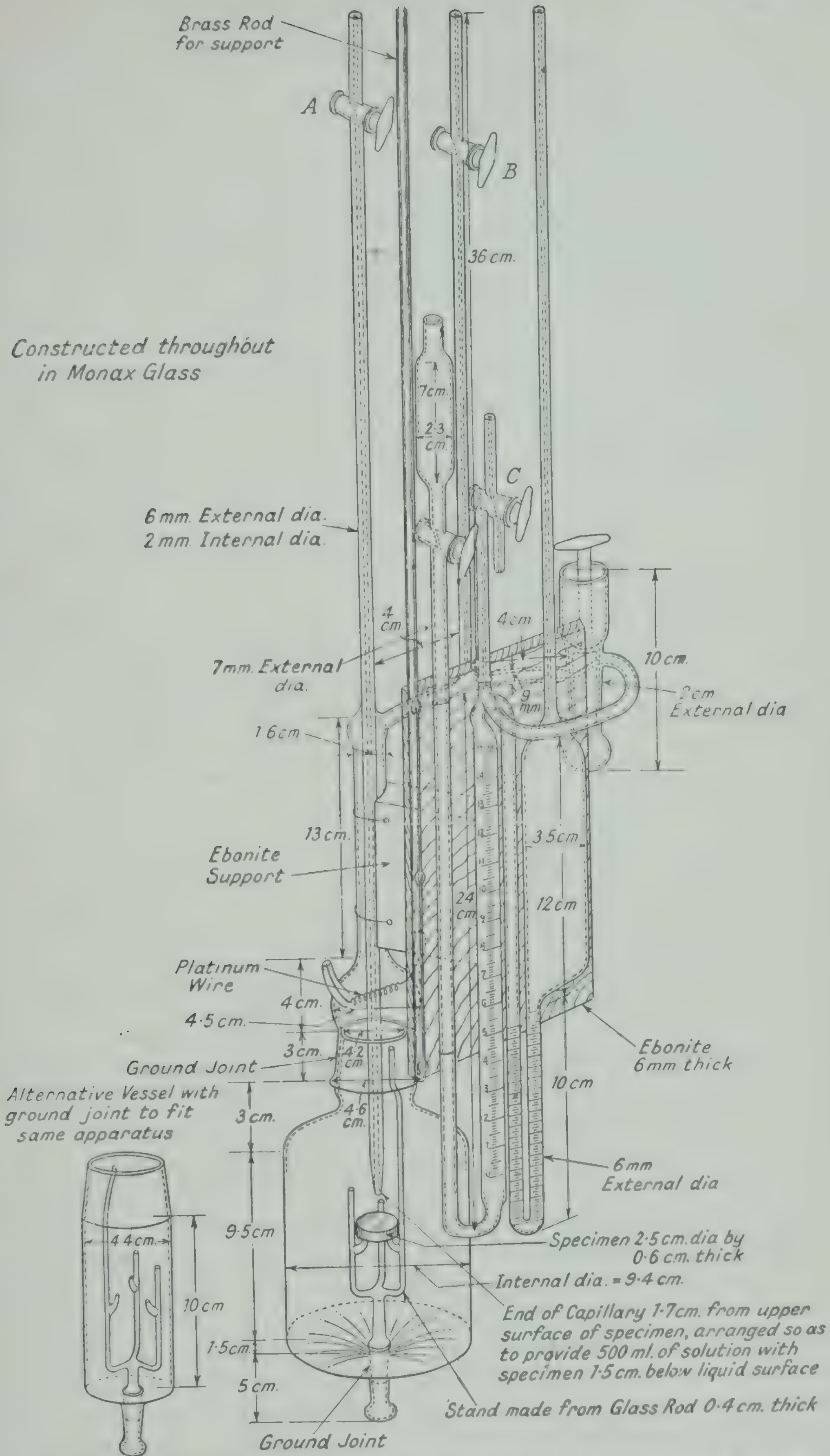

Brass Rod
for support
A
B
36 cm.
Constructed throughout
in Monax Glass
7cm.
2·3
cm.
C
6 mm. External dia.
2 mm. Internal dia.
4
cm.
4 cm
7mm. External
dia.
9
mm
10 cm.
2 cm
External dia
1·6 cm
13 cm.
3·5 cm
Ebonite
Support
24
cm
12 cm
Platinum
Wire
4 cm.
4·5 cm.
3 cm.
4·2
cm
Ground Joint
Ebonite
6mm thick
10 cm
Alternative Vessel with
ground joint to fit
same apparatus
3 cm.
4·6
cm.
6mm
External dia
4·4 cm.
9·5 cm
Specimen 2·5 cm. dia by
0·6 cm. thick
Internal dia. = 9·4 cm.
10 cm
End of Capillary 1·7cm. from upper
surface of specimen, arranged so as
to provide 500 ml. of solution with
specimen 1·5 cm. below liquid surface
1·5 cm.
5 cm.
Stand made from Glass Rod 0·4 cm. thick
Ground Joint

FIG. 44.—Apparatus for Measuring Corrosion by Absorption of Oxygen (G. D. Bengough, J. M. Stuart, A. R. Lee and F. Wormwell).

By exposing a series of specimens for different times, curves may b plotted indicating progress of attack with time; these serve to distinguish cases where attack stifles itself from those where it does not But, since a series of nominally "identical" specimens do not alway suffer corrosion at the same rate, the points may not fall well on a singl curve, and there is obvious advantage in a method providing a complet curve from a single specimen. Where a metal is attacked by acid, evolvin hydrogen, the volume of the hydrogen liberated furnishes such a curve

In corrosion of the oxygen-absorption type, the volume of oxyge disappearing has been used by Bengough in the same way; since a littl hydrogen is generally evolved even from neutral solutions, it is necessary periodically to burn this hydrogen by means of a heated platinum wire, the contraction of volume being noted. Bengough's apparatus is shown in Fig. 44; the specimen is a metallic disc supported horizontally on thre glass points, a known distance below the surface of the liquid. The space above the liquid is filled with oxygen, the disappearance of which is followed in the burette. Corrosion-time curves obtained with the apparatus are reproduced in Figs. 48 and 49 (pp. 90 and 91).

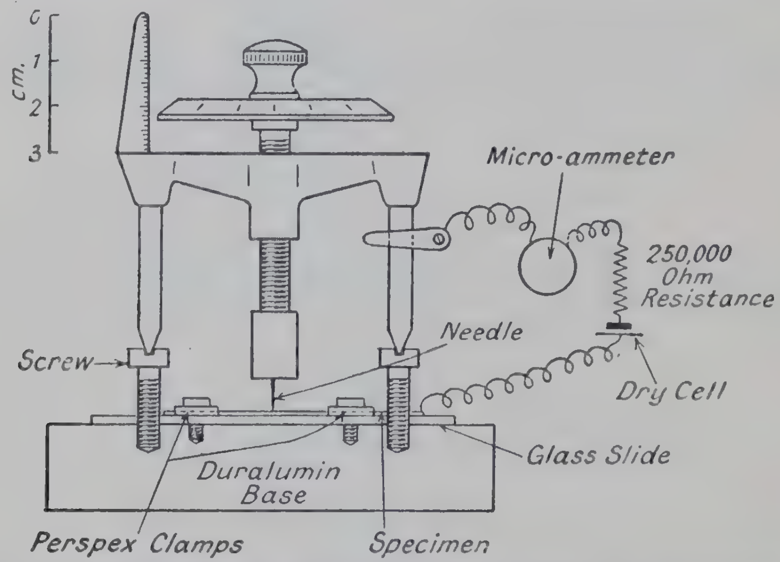


Fig. 45.—Apparatus for Measuring the Depth of Penetration of Localized Corrosion (R. S. Thornhill).

A complete time-corrosion curve can be furnished from a single specimen of wire (preferably a spiral) if its electrical resistance is measured from time to time during exposure to corrosive influences. Such information will only agree with gravimetric results if the corrosion is absolutely uniform, and any discrepancy between the two methods may provide useful evidence of localized attack.

The loss of tensile strength, of elongation or of fatigue strength brought about by corrosion is of great importance to engineers. Here again, an apparent disagreement with the results of gravimetric studies points to some form of localized attack; cracking will affect mechanical properties more than pitting.

Pitting, however, possesses practical importance, since it determines the time which pipes or containers can survive before they become perforated. An electrical micrometer used by Thornhill [142] to measure the depth of penetration at pits or patches of localized corrosion is shown in Fig. 45. The needle is screwed down until it touches the base of a pit; when contact is made, an electric circuit is established, and a deflection of the microammeter shows that the bottom has been reached; comparison with readings obtained at uncorroded places outside the pit gives the depth.

Atmospheric Attack

Exposure to Air containing Volatile Electrolytes. Certain early experiments carried out by the author [33a] on various metals exposed to air containing the fumes of volatile reagents may serve to illustrate the factors governing atmospheric attack, although the concentrations of the corrosive substances were far higher than usually occur even in a polluted industrial atmosphere. The experiments were conducted in vessels of the form commonly used as desiccators, the specimens being placed on a false bottom in the upper part, and the volatile liquid below; hydrochloric, sulphurous, carbonic acids, hydrogen sulphide solution and ammonia were used in different vessels; one vessel contained pure water. The liquid evaporated by day and condensed on the specimens by night. Pure water and even carbonic acid solution produced little real change, beyond a little dulling in some cases, and tiny rust spots on the iron. The other reagents caused appreciable attack on most metals, although lead resisted the vapours from sulphurous acid, tin underwent little change over any liquid apart from slight discoloration, whilst aluminium remained unaffected except over hydrochloric acid, which on some specimens produced a feathery growth—probably from weak spots in an otherwise protective oxide film. Iron over hydrochloric acid assumed a frosty aspect; when subsequently taken out into the ordinary damp atmosphere it absorbed moisture (ferrous chloride being hygroscopic) and developed rust; the same acid produced interference colours on lead, but the attack was only superficial.

The most serious action was observed where the surface absorbed moisture, and remained visibly wet even by day when, in the absence of hygroscopic bodies, water would have evaporated. Zinc exposed over hydrochloric acid developed a colourless syrup, and was rapidly eaten through; here the hygroscopic substance was zinc chloride. Sulphurous acid caused rapid rusting on iron, presumably because the portion adsorbed on the surface became catalytically oxidized to sulphuric acid, which attracted moisture; the brown-black deposit was 0·1 mm. thick after 2 weeks. Zinc also became damp, and after two weeks was covered with a pasty deposit 0·2 mm. thick. Nickel after two days began to shed a pale green liquid and the surface became covered with a green-black layer containing more sulphite than sulphate; this was 0·5 mm. thick after two weeks. Ammonia, which left iron bright and unchanged, owing to the alkaline reaction, produced a marked change on copper; a violet liquid containing the ammine $[Cu(NH_3)_4](NO_2)_2$ ran off the surface; here again catalytic activity will be noticed, ammonia being oxidized to the state of nitrite.

Copper Exposed to Air containing Moisture and Sulphur Dioxide. Vernon [149] carried out a series of quantitative experiments on copper, which he found to be little altered by air containing either sulphur dioxide or moisture alone, but to undergo serious alteration when both were present. One set of experiments, with the sulphur dioxide concentration kept at 10% gave results represented by the curves of Fig. 46. It will be noticed that so long as the R.H. does not exceed 63% the corrosion is slow, but that at 75% the attack is considerable. Apparently at this value the adsorbed sulphur dioxide can collect sufficient water for catalytic oxidation to sulphuric acid, which in presence of oxygen attacks copper readily. Several other cases (pp. 74, 85) are known of this sudden rise of corrosion velocity at a certain *Critical Humidity.*

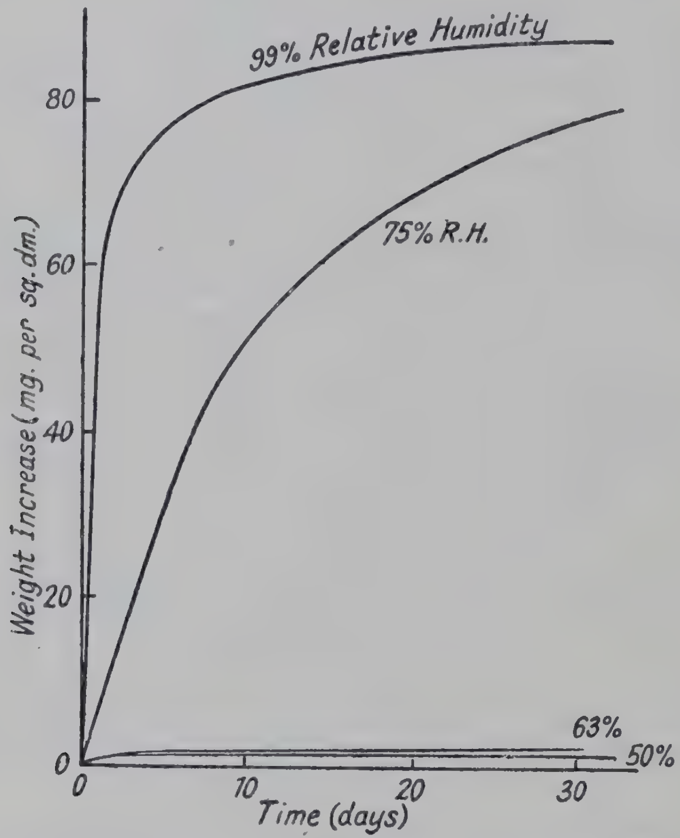


FIG. 46.—Corrosion of Copper by Air containing 10% Sulphur Dioxide and Different Degrees of Moisture (W. H. J. Vernon).

When the moisture content was kept constant whilst the sulphur dioxide was varied, Vernon found that 0·9% sulphur dioxide produced less corrosion on copper than either higher or lower contents; the film produced at this particular concentration was found to be normal $CuSO_4$, which provided better protection than either the basic sulphate film formed at lower sulphur dioxide concentrations or the more acidic film formed at high concentrations.

Copper Exposed Outdoors. It is well known that many ancient copper roofs carry a beautiful green patina. In urban districts this appears only after some years, its development being favoured by wind and rain. Vernon and Whitby [155] report that, in the opening stages, the deposit is a dark aggregate of sulphide, oxide and soot; the final green patina is formed in part by the action of sulphuric acid in the soot, and partly by the oxidation of copper sulphide. Evidently the changes are complicated. Analyses by Vernon and Whitby of the products from ancient green roofs show that those 70–300 years old carry basic copper sulphate $CuSO_4.Cu(OH)_2$ (*brochantite*), usually with a little basic carbonate $CuCO_3.Cu(OH)_2$ (*malachite*). The samples from newer roofs show a lower basicity, and even normal copper sulphate may be present. Near the sea coast, basic chlorides are found, their composition usually approximating to $CuCl_2.3Cu(OH)_2$ (*atacamite*) in the oldest deposits. In most coastal towns, sulphates seem to exceed chlorides in amount. On copper or bronze articles exposed for centuries in salt or alkaline desert, chloride and carbonate may become the most important constituents of the deposit formed on the surface. Copper nitrate, basic or normal—due to electric discharges—has been reported on electrical equipment.

Outdoor Tests on Non-Ferrous Metals. The results of an extensive series of tests carried out by Hudson [88] for the British Non-ferrous Metals Research Association on specimens either fully exposed to the rain or placed in Stevenson screens are summarized in Table X. The least resistant material tested (zinc) corrodes about 5 times as fast as the most resistant material (80/20 nickel chromium); corrosion is more rapid in the urban atmosphere of Birmingham (Post Office roof) or the marine atmosphere of Southport (golf course) than in the rural atmosphere of Cardington.

The numbers suggest that under normal conditions non-ferrous materials resist corrosion remarkably well, but it is right to point out that special circumstances exist where attack is more rapid. If rain falls on a sloping roof of slate or glass exposed to coal smoke or acid fumes, it will pick up much acid as it descends, and if it runs off at a limited number of points on to zinc or "galvanized" (zinc-coated) iron, there may be rapid attack at these points, which receive, as it were, far more than their proper "ration" of acid. Moreover, although, as explained on p. 75, zinc or zinc-coated iron resists fine salt spray, the state of affairs is very different if large drops of salt water lodge between sheets of galvanized iron, piled near the coast or in the hold of a ship. In such a situation, the mechanism described on p. 28 produces anodic attack in the centre of the drop, leading to the formation of zinc chloride, whilst sodium hydroxide is formed at the cathodic zone around the periphery; where they meet, zinc hydroxide will certainly be precipitated, but in a membranous form growing out at right angles to the surface and incapable of stifling attack.

Values of the Average Thickness of the Corroded Layer deduced f

pe

Material	Cardington			Bournville	
		Complete Exposure			Compl Exposu
	Stevenson Screen: Weight Increment Tests (Wire)	Resistance Tests (Wire)	Loss in Weight Tests (Plates)	Stevenson Screen: Weight Increment Tests (Wire)	Resistance Tests (Wire)
80/20 nickel-chromium	30	78	17	54	133
Lead	—	—	56	—	—
Arsenical copper	15	187	63	36	268
High-conductivity copper	16	139	76	37	242
70/30 nickel-copper	59	172	57	134	343
Cadmium-copper (0·8% Cd)	15	150	78	34	264
Nickel	64	168	45	97	274
Aluminium bronze (3·5% Al)	27	160	82	56	257
"Silicon bronze"	—	178	76	—	269
80/20 copper-nickel	36	187	83	72	218
Tin bronze (6·3% Sn)	19	145	96	42	205
70/30 brass	38	202	81	69	359
High-purity zinc	35	—	117	106	—
Ordinary zinc	—	—	113	—	—
60/40 brass	—	—	95	—	—
"Compo wire" (brass)	107	156	—	240	343
Mean (omitting the brasses)	32	156	74	67	248

s obtained by each Experimental Method in Millionths of an Inch

Hudson)

	Wakefield		Birmingham			Southport			Average for the Five Stations				Ratio of Value deduced from the Loss in Weight Test to that deduced from the Resistance Test	Ratio of Value deduced from the Resistance Test to that deduced from the Stevenson Screen Test
	Complete Exposure		Stevenson Screen: Weight Increment Tests (Wire)	Complete Exposure		Stevenson Screen: Weight Increment Tests (Wire)	Complete Exposure		Stevenson Screen: Weight Increment Tests (Wire)	Complete Exposure		Loss in Weight Tests (Plates)		
	Resistance Tests (Wire)	Loss in Weight Tests (Plates)		Resistance Tests (Wire)	Loss in Weight Tests (Plates)		Resistance Tests (Wire)	Loss in Weight Tests (Plates)		Resistance Tests (Wire)	Tensile Tests (Wire)			
	175	62	111	311	85	48	137	26	60	167	120	47	0·28	2·8
	—	74	—	—	145	—	—	70	—	—	—	84	—	—
	350	141	126	353	154	43	366	125	54	305	312	116	0·38	5·6
	371	156	116	302	158	39	383	148	50	288	288	131	0·46	5·8
5	478	134	376	656	243	127	394	113	170	408	389	134	0·33	2·4
2	402	160	120	350	179	39	407	147	50	314	—	135	0·43	6·3
7	560	218	245	564	230	141	325	111	155	378	359	140	0·37	2·4
0	344	169	170	410	229	56	443	151	74	323	252	150	0·46	4·4
—	385	180	—	342	228	—	382	179	—	311	242	157	0·51	—
4	352	206	204	361	213	89	304	179	101	284	355	162	0·57	2·8
9	270	189	151	305	243	46	308	212	61	247	145	174	0·70	4·0
8	548	205	172	594	316	92	506	195	90	442	1030	191	0·43	4·9
8	—	261	280	—	376	81	—	199	124	—	—	230	—	—
—	—	258	—	—	388	—	—	207	—	—	—	231	—	—
—	—	235	—	—	408	—	—	238	—	—	—	233	—	—
47	449	—	719	721	—	221	446	—	327	424	2208	—	—	1·
90	368	170	190	395	221	71	345	144	90	302	274	146	0·45	4·

Outdoor Tests on Ferrous Materials. Some of Hudson's results[89, on steel specimens exposed for the Iron and Steel Institute Corrosion Committee are shown in Table XI, along with corresponding results for zinc

TABLE XI

Corrosion in One Year Expressed in Millionths of an Inch (J. C. Hudson)

	Ingot Iron	Zinc
Khartoum	28	22
Abisko, Sweden	158	36
Aro, Nigeria	339	57
Basrah	400	28
Singapore	517	46
Apapa, Nigeria	654	38
Llanwrtyd Wells	1888	118
Calshot	2104	121
Dove Holes Tunnel (Up Side)	2841	3609
Dove Holes Tunnel (Down Side)	3066	3449
Motherwell	3137	180
Woolwich	3472	146
Sheffield	3888	576

except in the tunnel, steel suffers attack much more rapidly than zin (and hence than other non-ferrous materials), but here again it i

TABLE XII

Relative Corrosion in Five Years' Exposure Tests (J. C. Hudson)

Material	Calshot (Marine)		Dove Holes Tunnel (highly polluted) as Rolled	Sheffield (Industrial)	
	As Rolled	De-scaled		As Rolled	De-scaled
Steel X (0·02% Cu)	100	100	100	100	100
Steel Y (0·2% Cu)	81	92	—	80	83
Steel Z (0·5% Cu)	78	87	—	79	82
Slagless Wrought Iron (no copper added)	—	—	98	155	131
Slagless Wrought Iron (0·6% Cu)	—	—	92	68	67
Staffs. Wrought Iron (no copper added)	113	95	79	77	78
Scottish Wrought Iron (0·12% Cu)	102	93	90	73	66
Ingot Iron	148	120	96	104	106

quickest in industrial atmospheres containing oxides of sulphur. Other results by Hudson, collected in Table XII, indicate how copper in steel increases the resistance; probably, as explained on p. 57, copper serves to fix sulphur and prevent stimulation of attack by hydrogen sulphide (formed by acid substances in the air acting on sulphides in ordinary steel). It is commonly thought to produce a more compact protective type of rust, but this may itself be connected with the slower anodic attack.* If in addition to copper, chromium is present, the life is further prolonged.

Wrought iron containing slag shows good resistance to atmospheric attack, but that without slag has a relatively short life unless it contains copper. Probably, as suggested on p. 57, the behaviour of wrought iron is due to the sulphide being mainly found in the slag layers, with the intervening iron relatively pure. Thus corrosion starting from points on the face of a rolled sheet advances inwards much more slowly than on steel; when a slag layer or slag string is tapped, attack may become faster, but tends to turn sideways, so that the dangerous inwards penetration still remains slow. Whatever the cause, numerous examples are on record of wrought-iron structures which have remained in good condition over very long periods.

Indoor Tests on Non-Ferrous Metals. Vernon[147] found that copper exposed indoors obeyed the parabolic law, the weight increase W in time t being given by $W^2 = Kt$. Zinc obeyed the rectilinear law, $W = Kt$, but as shown in Fig. 16 (p. 17), the value of K varied between experiments started on different dates, although in each experiment it remained remarkably constant, despite the fact that atmospheric conditions were varying. This suggests that *the course of attack is determined by the conditions prevailing at the commencement of exposure*, and observations by American and German investigators confirm this important principle.

Indoor Tests on Ferrous Materials. Vernon's researches [151] showed that the spots of rust which appear on iron exposed in a room are connected with dust particles settling on the surface. Various components of dust behave differently; silica is harmless, ammonium sulphate promotes attack, whilst carbonaceous particles (soot) only stimulate corrosion if sulphur compounds are adsorbed on them. If iron or steel is exposed in a muslin cage which, whilst allowing access of air, prevents dust particles from reaching the metal, the spots of rust, which would otherwise appear, are avoided; if after exposure for eleven months in such a sheltered situation, the iron is exposed to ordinary air containing dust particles, the rusting is far less serious than that of iron freshly exposed to dusty air, since the invisible oxide film built up during the first stage confers a measure of protection.

Vernon found two critical humidities on iron exposed to air containing sulphur dioxide; if the moisture content was gradually raised, rusting commenced when the humidity reached about 60%, and greatly increased at about 80%. The causes still remain somewhat in doubt.

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* Redeposition of metallic copper may provide an intimate mosaic of anodes and cathodes, leading to the precipitation of more compact rust than is formed when the anodes and cathodes are large areas.

Stainless Steels.[111] Whilst copper steel and wrought iron suffe atmospheric corrosion more slowly than ordinary mild steel, they canno be called non-rusting. To ensure retention of brightness during ordinar atmospheric exposure, it is necessary to add *chromium* in considerabl quantities. *Stainless cutlery steel* contains about 14% of chromium an 0·3% of carbon ; it is usually hardened about 950° C. followed by quenching (or sometimes air-cooling) and is subsequently tempered about 200° C the structure being then essentially martensitic. A similar alloy low i carbon and consequently softer, known as *Stainless Iron*, is used i structural engineering.

Where no hardening is needed, an enhanced resistance to atmospheri attack can be obtained from austenitic (γ-iron) alloys with larger chromium contents ; these have been mentioned on p. 65 in connection with aci resistance, and are sold under various trade names (*Staybrite*, *Alleghan Metal*, *Anka*, etc.) ; a favourite composition is 18% chromium, 8% nicke —the latter metal serving to ensure the austenitic condition ; the pric of nickel has encouraged efforts to replace it in part by other austenite stabilizers, such as manganese or even nitrogen. The austenitic state i obtained by heating to about 1100° C. and cooling rapidly. If, as may happen during welding, an 18/8 alloy is heated to about 700°, the chromium at the grain boundaries tends to separate out as carbide, leaving an impoverished network, so that the alloy becomes susceptible to intergranular attack ; as explained on p. 113, this is largely overcome by adding other elements, such as titanium and tungsten ; recently it has become common to use columbium (niobium) in place of titanium.

The austenitic alloys are much more resistant to attack than stainless cutlery steels but cannot be hardened. There is, however, a type of alloy, containing 16–20% chromium and 2% nickel, which excels the cutlery type in resistance and yet possesses hardening properties ; it has proved useful in aircraft. One commercial brand is known as *Two Score*. It is usually hardened at 950° C., and tempered at 600–650° C., which leaves a ferritic structure containing minute particles of carbide.

Corrosion of Buried Metal Work

General. Conditions existing in the soil may vary between something comparable to atmospheric exposure and what is almost equivalent to complete immersion. A metal pipe buried in very open, sandy ground has a considerable portion of its surface exposed to air. Oxygen gains sufficient access to ensure that ferric products are formed close to the metal ; a film of rust may soon appear on the surface, but it frequently stifles further attack. In waterlogged soils, free oxygen is deficient, and, in the absence of those bacteria which make the oxygen of sulphates available for the corrosion reaction, there is only slow attack ; but whatever attack does occur is not likely to stifle itself, since the ferrous compounds are only converted to ferric at a distance from the surface.

Soils of intermediate character may produce corrosion which is localized, and accordingly intense. If air pockets are present, either as a natural feature of the soil, or produced artificially when the soil is thrown back into a trench after the laying of a pipe-line, so that spaces are left in between the individual spadefuls, differential aeration currents may flow ; oxygen is taken up at the air pockets and attack is directed on the places where the soil presses on the metallic surface. The American investigators of soil corrosion, especially Denison and Darnielle,[26] have demonstrated the currents set up by the cell

Steel | Wet Soil without air | Same Soil, drier, with air | Steel

Such cells are stated to produce E.M.F.s exceeding 0·5 volts.

Cells of the type

Steel | Soil A | Soil B | Steel

may be set up where a pipe passes from one soil to another, and there is a special risk of corrosion if a pipe is buried at a level representing the boundary between two horizontal soil-strata. Attack is sometimes met with where a steel or lead pipe passes near salt-pockets or mineral springs, whilst different constituents of the soil may themselves set up corrosion currents ; thus where lead is buried in a ground containing lumps of chalk, local attack may occur, probably because the chalk precipitates lead as carbonate and thus keeps the $Pb^{\cdot\cdot}$ concentration low locally, bringing about the concentration cell

Lead | Dilute $Pb^{\cdot\cdot}$ | Concentrated $Pb^{\cdot\cdot}$ | Lead

Steel pipes buried in cinders, especially those containing sulphur, are rapidly corroded.

The rapid attack on steel pipes and lead sheathing due to stray currents from tramways was discussed on p. 43.

Sulphate-reducing Bacteria. Even more dangerous than the purely chemical or electrochemical types of attack on pipes is the action of the sulphate-reducing bacteria known usually as *Vibrio desulfuricans* (also as *Spirillum*, *Spirovibrio* or *Microspira desulfuricans*). These organisms can flourish only in anaerobic soils, like waterlogged clay, containing sulphates and organic matter. Soils containing no free oxygen are usually non-corrosive, if sterile, but the organisms mentioned enable sulphates to act as hydrogen-acceptors, with reduction to sulphides. Thus soils which are insufficiently acid to produce appreciable attack of the hydrogen-liberation type, and which contain too little oxygen for the aerobic types of corrosion, nevertheless set up serious attack in presence of these bacteria. Instead of rust, a black coloration due to iron sulphide is found around iron or steel suffering from the bacterial type of destruction (but black coloration may also be caused in other ways, e.g. when iron is precipitated as magnetite). Both cast iron and steel pipes can be affected by bacterial action, the attack being often localized and sometimes very rapid. On cast iron, the graphite network remains unchanged, so that the pipe may appear undamaged, until tested with a knife-point, when portions will be found to be very soft. The subject was originally studied in Holland by von Wolzogen Kühr. Bunker,[17] who has made an extensive study of the bacterial wastage of British pipes, reports cases where cast iron pipes 1 cm. thick have been perforated in clay soils in nine yea With steel, there can be no graphitic corrosion, and the actual rate penetration may be slower ; on the other hand, steel pipes are general thinner than those of cast iron.

Prevention of Corrosion of Pipes. Since steel suffers little corrosi in open soils, it is possible to dig a trench, fill it with porous brick, grav or even sand (if quite free from clay), thus isolating the steel from th corrosive ground around ; chalk in the sand is said to add to its protecti character, and one authority recommends surrounding the pipe with cla to which lime has been added. In another method, usually effective bu expensive, the pipe is set centrally in a long " box " which is then fille with a cement or concrete surround. Pipes externally or internal covered with cement mixtures are available.

Another plan is to coat the pipe with compositions containing bitume or tar (tar from horizontal retorts is superior to that from vertical retorts In relatively mild conditions mere painting with a solution of tar whic dries by evaporation may suffice. A better plan is to dip the whole pip into a hot mixture giving a coat which becomes solid on cooling. Fo really corrosive soils, thick coatings of a bituminous or tarry base fortifie with a filler such as ground limestone, silica, mica or slate are necessary

For many years it has been customary, in this country, after applyin a priming coat of tar or bitumen solution (which dries by evaporation to wind the pipe with bandages of hessian soaked in hot tar, which harder on cooling. Unfortunately many soils contain cellulose-destroyin bacteria, which rot the hessian, so that wrapped pipes occasionally behav worse than unwrapped ones ; the situation is made worse by the fact tha the products of bacterial rotting, although not directly corrosive, provid food for the sulphate-reducing bacteria mentioned above. In such case it may be better to use asbestos felt saturated with the bitumen or ta Attempts have been made to arrest the trouble by incorporation of substances designed either to kill the cellulose-destroying or the sulphate reducing variety of bacteria ; it is too soon to judge whether succes can be achieved on these lines.

By coating steel pipes with zinc, considerable increase in life can b obtained, except in acid soils, for which galvanized pipes are unsuited Logan's extensive tests[99] on soil corrosion in America showed that i most soils, a zinc coating of 2·8 oz./ft.^{2} prevented appreciable rusting fo ten years. Lead-coated pipes behaved well for a time, but when onc the coating was eaten through, attack proceeded rather fast ; the contras between zinc and lead is not surprising, since zinc is anodic to iron whereas lead—in many environments—is cathodic (see p. 48).

Attempts to avoid corrosion of steel pipes by altering their compositio have not been very successful. Logan's tests suggest that there is comparatively little difference in the behaviour of mild steel, wrought iron and numerous low-alloy steels. High-silicon iron and austenitic chromium nickel steels show high chemical resistance, but the former is very brittl and the latter expensive. Among non-ferrous materials, lead and coppe ipes are chemically more stable than steel, but their mechanical properties re less favourable; recent work by von Wolzogen Kühr suggests that oth copper and lead are seriously attacked in made-up ground containing arbonaceous matter.

Corrosion of Immersed Metals

Iron. The most extensive laboratory studies of iron and steel fully mmersed in salt solutions (particularly potassium chloride), with oxygen bove the liquid, have been carried out by Bengough and his colleagues, Stuart, Lee and, particularly, Wormwell,[8] using the apparatus shown in Fig. 44 (p. 77). Some of the experiments lasted many years, and the iron became covered with a layer of granular magnetite itself overlaid with flocculent ferric hydroxide. During considerable periods, constant corrosion rates prevailed; changes of velocity came about comparatively suddenly—evidently through changes in the physical state of the corrosion product, which would affect the amount of oxygen reaching the metal (or reaching the magnetite, if, as Herzog [76] has suggested, the magnetite layer acts as cathode towards the iron as anode).

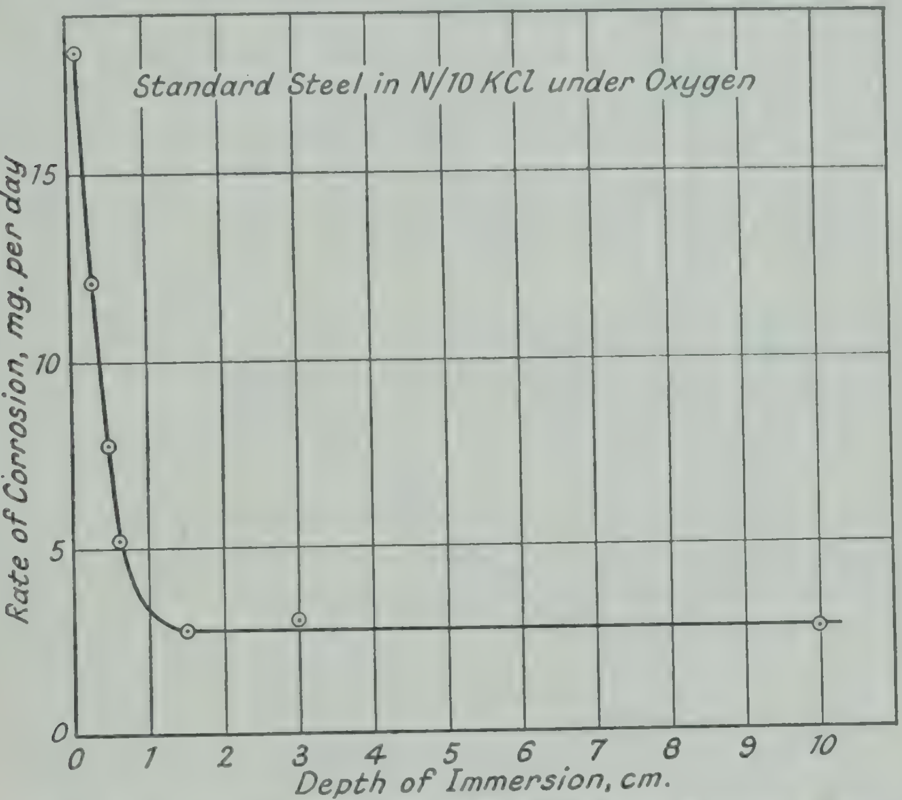


FIG. 47.—Influence of Depth of Immersion on Corrosion Rate (G. D. Bengough, A. R. Lee and F. Wormwell).

Bengough's results [10] demonstrate that the speed of corrosion is limited by the rate at which oxygen reaches the corroding system. The replacement of air by oxygen increases the rate of attack, whilst the raising of the oxygen pressure above the atmospheric value causes a further increase in corrosion, unless the specimen is exposed to the high-pressure oxygen *before* the salt solution is introduced ; in the latter case, the iron becor partially passive, and the rate of corrosion is slowed down.

By increasing the cross-section of the containing cell (keeping specimen-size constant), a greater rate of entry of oxygen becomes possil so that the rate of corrosion is speeded up. On the other hand, an incre in the size of the specimen (under a certain range of conditions) har increases the total corrosion (so that the intensity of attack is actua diminished). This is easily understood, since, if a small specimen consume all the oxygen reaching the appropriate level in the vessel large specimen will obtain no more.

Where the upper face of the specimen is placed only a short distar below the liquid surface, the corrosion rate diminishes as this distanc

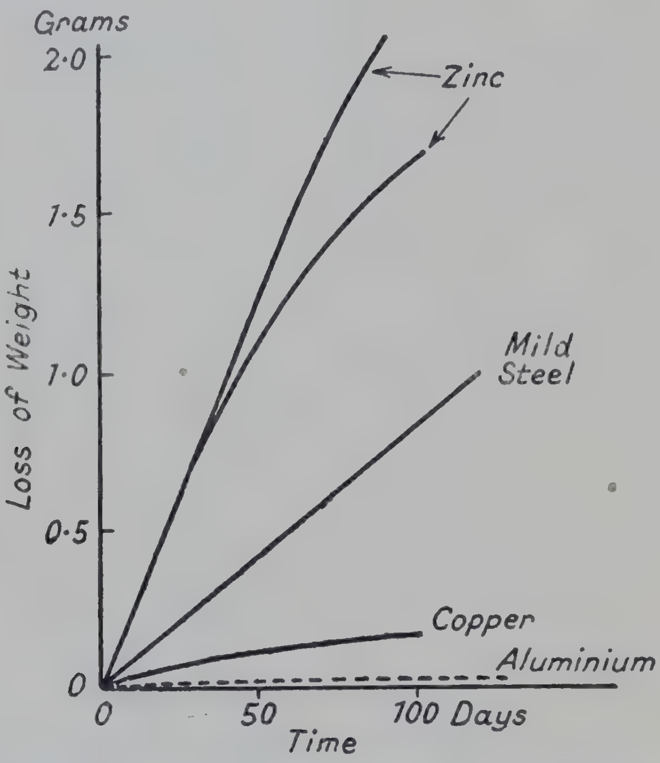
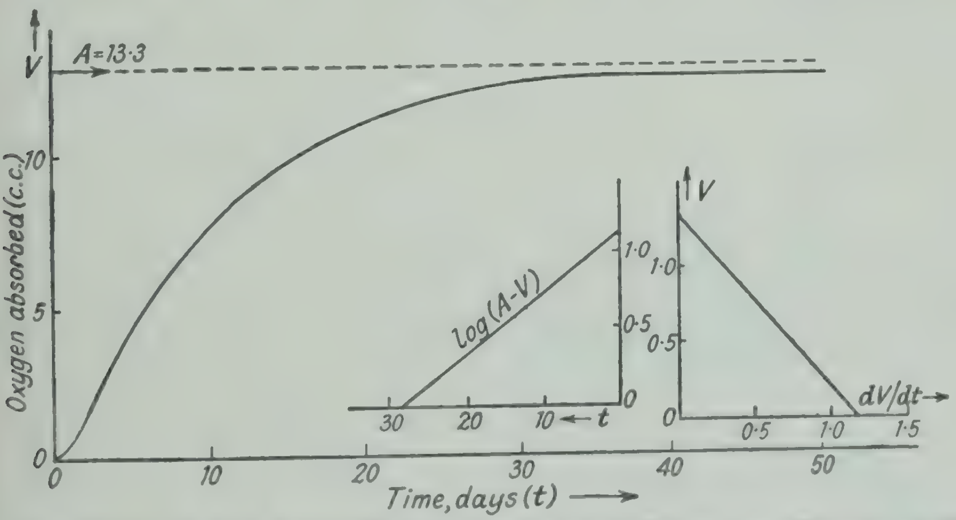


FIG. 48.—Corrosion of Metals fully immersed in N/2 Sodium Chloride in presence of Oxygen (G. D. Bengough and F. Wormwell).

increased (Fig. 47). But at depths of immersion exceeding 1·5 cm., corrosion rate ceases to fall off further, and it is clear that the mechani of supply of oxygen to the metal must have altered. At shallow imm sion, oxygen probably reaches the metal by *diffusion* downwards acr the liquid layer separating gas from metal, so that the corrosion r diminishes with increasing depth, whereas at deep immersion, oxyg travels down by *convection currents*, which are almost independent depth. There is still some doubt regarding the origin of the convect currents in Bengough's experiments, but apparently they are influenc by the nature of the corrosion product, since, notwithstanding that ir can use up, in fairly concentrated salt solutions, all the oxygen reachi it, yet zinc is corroded more quickly than iron (Fig. 48), suggesting tha ceives a more ample supply of oxygen ; the fact that on iron some of e oxygen is used up in converting ferrous to ferric compounds cannot lly account for the discrepancy. Copper and aluminium corrode far ore slowly, and probably do not attain the maximum rate permitted by nsiderations of oxygen-supply ; the resistance of copper is connected th its intrinsically noble character, but that of aluminium is due to the otective character of the alumina film.

In the actual corrosion of immersed steel work, the oxygen will usually ach the metal through the motion of the water (e.g. where it runs through tank or a pipe). In other cases, there may be convection currents set by temperature differences. In the rare event of the complete absence mechanical stirring and of thermal convection, convection currents uld still be set up by the difference between the specific gravities of the rrosion products and the corroding medium respectively (which differ- ice, however, is not so large as might be supposed, since rust and other droxides contain a great deal of water) ; in absence of other factors, e heat evolution connected with polarization or the heat generated by the rrosion currents (small but non-uniform) might conceivably maintain rculation.

Zinc. The corrosion of partly immersed zinc plates has been discussed p. 31. The attack upon horizontal totally immersed zinc was studied detail by Bengough.[8] At high salt concentrations, the corrosion rate as controlled by the rate of oxygen-arrival, and fell off with rising salt ncentration, since this depressed the oxygen-solubility. At very low tassium chloride concentrations, it was controlled by the salt concen- ation, since chlorine ions were needed to give a soluble anodic product. t these concentrations, it was found that the corrosion rate diminished ith time (Fig. 49), and that this was due to the removal of chlorine in



IG. 49.—Corrosion of Zinc fully immersed in N/10,000 Potassium Chloride at 25·0° C. (G. D. Bengough, J. M. Stuart and A. R. Lee).

he secondary corrosion product. Clearly if the zinc chloride and sodium ydroxide formed at anodic and cathodic regions respectively interacted to form zinc hydroxide, then the chlorine ion concentration would rema undiminished. Actually it appears that a basic chloride is thrown dow so that chlorine is removed in proportion to the total corrosion. If t corrosion rate is proportional to the chlorine remaining in the solutio it follows that

$$dV/dt = k_1(C_{Cl} - k_2V)$$

where V is the corrosion (expressed as the volume of oxygen absorbe at time t, C_{Cl} the original chloride concentration, and k_1 and k_2 constan Writing A for C_{Cl} / k_2 and K for k_1k_2 we have

$$dV/dt = K(A - V)$$

or

$$V = A(1 - e^{-Kt})$$

The straight lines obtained when dV/dt is plotted against V or log (A — against t (see insets in Fig. 49) show that this relation governs the situatio

In addition to the oxygen-absorption type of corrosion, a little hydrog is evolved during the corrosion of zinc (especially impure zinc); Be gough's numbers show that on any specimen the rate of hydrogen-evoluti is at any moment proportional to the total corrosion (due mainly to t oxygen-absorption type) which has occurred up to that momer Evidently the hydrogen-evolution is due to the redeposition of metal impurities of low overpotential which form cathodes on which hydrog can easily be evolved; the amount of such impurities will depend on t total corrosion, explaining the proportionality mentioned.

Tin. Whilst on iron (or zinc) placed in (say) potassium chlori solution the main anodic product will, almost from the first, be a solul chloride, the state of affairs is different on tin, which forms eas hydrolysing salts. Here the rule propounded on p. 39 predicts that neutral potassium or sodium chloride the anodic reaction will invol (OH)′ ions rather than Cl′ ions, and that hydroxide will be formed ur the acidity produced by the loss of OH′ is sufficient to make the formati of a soluble tin salt the easiest reaction. Consequently the attack salt solutions on tin is very slow compared to that on iron and zinc.

This explanation was developed by Hoar [79] to interpret his observatio of the corrosion of tin rectangles immersed vertically in M/10 potassiu chloride. At first, the only visible change is a nearly even thickening the oxide film (as indicated by interference tints); electrical measu ments (see p. 73) show that healing of any weak places in the film occurring. It is thought that the healing is due to the anodic formati of insoluble tin hydroxides within the pores. However, the removal OH′ ions must gradually make the solution within the pores acid, a when the p_H becomes low enough for soluble tin compounds to exi metal dissolution will begin to undermine the film around the origi pore. Corrosion can now start. "Black spots" containing stanno and stannic hydrated oxides grow quite rapidly at the sites of atta and soluble or colloidally dispersed tin compounds diffuse out, becomi precipitated on the film surface around the spots and producing a ser of concentric rings of interference tints, whose colours show that t recipitated film is thickest nearest the black spot. These black spots on in have long been known, and are formed in salt solutions yielding oluble tin compounds (chlorides, sulphates, nitrates, etc.), but not in ases where the tin compound would be insoluble (iodates, borates, errocyanides, etc.).

Aluminium. The author[34] observed similar coloured rings on pecimens of rolled aluminium partly immersed in chloride or sulphate olutions. They start at susceptible points, such as blemish marks, cut dges and points on the water-line, where colour rings are numerous and end to be elongated horizontally. The early colours are weak, but the econd and third order tints, which are very beautiful, can easily be seen f the specimen is taken out and dried ; one specimen, after seven days' mmersion, displayed the whole sequence from first order yellow to fifth rder red around one centre (see Table V, p. 4).

On abraded specimens, the corrosion product is at first adherent, onsisting of white points arranged along the scratch-lines. After a few lays non-adherent aluminium hydroxide (formed by interaction of the nodically formed aluminium chloride and cathodically formed alkali) ppears ; this happens more quickly in chloride than in sulphate solutions. After fifteen days there is much settled flocculent precipitate in chloride solutions and some in sulphate solutions, but the attack is much slower than that on iron and zinc. Schikorr[129] showed that both the anodic and cathodic products can themselves attack aluminium, evolving hydrogen.

Quantitative studies of pure aluminium in normal potassium chloride solution have been carried out by Champion,[19] using a modification of the Bengough-Wormwell apparatus (p. 77). Corrosion of the oxygen-absorption and hydrogen-evolution types were separately measured, but both were found to be governed by the same relation between the corrosion y and time t. In the early stages, the rate dy/dt increased with y according to the equation

$$dy/dt = \alpha y + \beta$$

and later decreased according to

$$dy/dt = -\alpha' y + \beta'$$

where α, α', β and β' were constants. Later a second rise and a second fall were experienced, but again dy/dt was a rectilinear function (positive or negative) of y. Champion ascribes the first increase to " the effect of corrosion products on corrosion ", and the subsequent fall to " the formation of a protective film ".

Cadmium. Experiments at Cambridge by Borgmann[14] on cast rods of cadmium showed that the main product is an adherent brown film, so that here again the attack is slow ; probably the explanation is to be found in the principle of p. 39.

Copper. Since cuprous chloride is sparingly soluble, the anodic corrosion product of copper in potassium chloride solutions remains attached to the surface. It does not, however, stifle attack entirely, possibly because some soluble cupric chloride is also produced. Th cuprous chloride is converted into cuprous oxide *in situ* by the alka diffusing from the cathode. In the author's experiments[34] on finel abraded specimens, the oxide film formed oval-shaped patches of ric colours, being thickest close to the points of origin. On coarsely abrade specimens, the matter was less adherent and contained both cuprou and cupric oxides. Corrosion was slow, but after some days loose gree matter appeared and settled to the bottom of the containing vesse This was probably a basic cupric chloride, formed by interaction betwee cupric chloride from the anode and sodium hydroxide from the cathod

Brass. Two types of brass are commonly met with in practic The 70/30 copper-zinc alloy, if carefully annealed, should consist of single α phase, although, if rapidly cooled from the fused state, trace of β phase may be present between the α grains. The 60/40 alloy alway contains both α and β phases.

Since zinc is a far less noble metal than copper, it might be expecte that, on immersing brass in sodium or potassium chloride containin oxygen, the zinc would first be corroded and the copper left in the metalli state. This can only occur, however, if there exist continuous filament of zinc atoms extending from the surface into the interior ; assumin sporadic distribution of the species, the continuity of such filament becomes increasingly unlikely as the content of copper in the allo increases. Consider the behaviour of an alloy consisting of two constituents A and B placed in a reagent capable of attacking the baser meta B (in the unalloyed state) but not A. In general, attack is only foun to occur if the proportion of B exceeds a certain amount, known as th *Parting Limit.* On fully annealed specimens, where the two species o atoms have assumed their most stable arrangement, the parting limi often occurs when one-half or one-quarter are of the noble variety, according to the reagent (see Table XIII).* With cold-worked metal, wher the arrangement will be disturbed and where the atoms, being mobile can probably change places at ordinary temperatures, the parting limi is less sharp.

TABLE XIII

COMPOSITIONS AT WHICH PARTING LIMITS ARE MET WITH (collected by U. Dehlinger and R. Glocker)

Alloy System	Percentage of Atoms of Nobler Metal
Copper-Gold	22 to 25·5%
Silver-Gold	24·5 to 32
Gold-Palladium	20 to 28
Copper-Gold	50
Silver-Gold	48 to 50·5

In brass the copper atoms are present in excess, and it is not surprisin that the attack is generally no quicker and sometimes slower than tha upon copper, suggesting that zinc atoms cannot easily leave the alloy unless copper atoms accompany them. Nevertheless, a certain slow "dezincification" of brass placed in sodium chloride solution seems to take place, especially in the β (zinc-rich) phase of an $\alpha\beta$ brass, or at the grain boundaries of insufficiently annealed α-brass, where relatively zinc-rich areas exist; at such places zinc passes into solution, leaving residual copper.

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* Theory would suggest that the parting limits should be sharper in alloy systems formin “ super-lattices ”.

When once a small amount of residual copper has been formed by local dezincification, and when once a small deposit of zinc and copper compounds (usually basic chlorides) has been formed locally by corrosion of *both* constituents of brass, then a cell can be set up which, once started, may produce serious local attack; this cell is

Brass | Sodium Chloride containing Copper Compounds | Copper

The brass will be the anode, and both zinc and copper will pass into solution:

$$Cu = Cu^{\cdot\cdot} + 2e$$
$$Zn = Zn^{\cdot\cdot} + 2e$$

At the cathode, copper will be deposited in amount equivalent to the copper entering the solution at the anode,

$$Cu^{\cdot\cdot} + 2e = Cu$$

whilst the passage of zinc at the anode is balanced by the reduction of oxygen at the cathode

$$O + H_2O + 2e = 2(OH)'$$

The final result is therefore the same as though only the zinc were attacked, and the E.M.F. driving the cell should be the same as for true dezincification; but, owing to the fact that there is no need to remove zinc atoms from the interior of a brass mass, the resistance is likely to be lower, and the action, once started, will proceed smoothly. The metallic copper thus formed will not be residual but redeposited; this smooth-running type of attack can only occur at a place where a reservoir of copper compounds has already been formed, and in this respect is autocatalytic; having started at a certain point, the action will continue there in preference to elsewhere.

For many years, it had been known that certain specimens of brasses merely underwent "complete corrosion" (leading to zinc and copper compounds in the proportions in which the metals occurred in the brass), whilst others of similar composition underwent "dezincification", real or apparent (leading to metallic copper). Bengough and his colleagues [11] were the first to discover that the principal factor determining behaviour was arsenic. If the brass contained a small quantity of arsenic, it resisted dezincification, although, if subjected to conditions sufficiently drastic to produce attack on the copper as well as the zinc, it would suffer "complete corrosion". Brass intended to resist dezincification by sea-water is often treated with arsenic, if that element is not already present in the copper employed for making the alloy. Alternatively the heat-treatment may be adjusted so as to avoid the zinc-rich areas where—it is thought—the action starts. Another plan is to reduce the zinc conten well below the customary 30%.

Experiments carried out at Cambridge by Fink[57] suggest that th copper formed during the corrosion of brass can be either residual o redeposited—the two types differing in physical condition—and that th arsenic acts by inhibiting the anodic process (true dezincification) and no the cathodic process (deposition of copper). Probably it forms a fil over just those zinc-rich spots where the action would begin.

Metal subjected to Rapidly Moving Water

General. Where water containing dissolved oxygen (and possibl entrained air bubbles) moves over a metallic surface, the rate of attac is not likely to be limited by shortage of oxygen. At places where som small foreign particle rests on the surface, a small area may be *locall* shielded from oxygen, and, under certain conditions, differential aeratio may set up attack, with the unaerated spot as a small anode, and th aerated area as a large cathode—the combination which is always likel to produce intense attack (p. 27). On bare steel, this localized corrosio is most probable if the water contains just sufficient inhibitor to preven attack at the free surface, but not at the shielded spot (where replenishment of inhibitor will be hindered). Intense attack on steel by wate not containing an inhibitor is most probable if the whole surface is covere with oxide (mill-scale) except for small breaks, which form the smal anodes in the large cathodic area.

Another form of intense localized attack may occur if the water carrie suspended sand which, impinging at some particular point, determine by the flow of the water, keeps damaging the film that would otherwis stifle attack, and leads once more to intense localized corrosion. Case of corrosion trouble due to sand suspended in water have been reporte from industrial plants—notably from beet sugar works. Impingemen of air bubbles or vacuum bubbles constitutes a somewhat special case and is considered on pp. 97, 98.

In the case of copper, another type of local attack may be set up i water passes rapidly over the surface at one point, but is relatively stagnan over the rest of the surface. The removal of copper ions from the poin of rapid motion keeps the ionic concentration locally low, and this poin will be permanently anodic to places where copper ions can accumulate Intense corrosion may thus arise, leading to perforation, e.g. on vertica externally cooled copper condenser tubes at a point opposite the water-inlet where the velocity is high.[35a] It might be thought that this effec should be obtainable with all metals. Actually metal ion concentratio cells—set up by differential stirring—can be demonstrated on lead. Bu on iron and zinc stirring has another effect, since the place where water i moving most rapidly receives the best supply of oxygen, and become cathodic rather than anodic. In general, the differential aeration effec will become more important, and the ion concentration cell less important, as we pass to base metals, and for various reasons the ion-concentration cell is rarely dangerous except in the case of copper.

Condenser Tube Corrosion. In boiler plants, the chambers used to condense the steam contain rows of tubes through which cold water is run (sea water is used in the case of marine boilers); the steam condenses outside. For the tubes 70/30 brass, sometimes containing 1% of tin, was at one time commonly used, although the $\alpha\beta$ type with about 40% zinc was also in favour, mainly on the Continent. The majority of the tubes enjoyed lives of many years, but occasionally a tube would become perforated in a few months—or even weeks. Failures were found by Bengough and his colleagues [11] to be of two main types:

(1) *Deposit Attack* occurs most often if the water speed is *slow*—as in many land condensers and some ships—at places where débris or some foreign body (sand, mud, coke, wood, shells or seaweed) has settled. The corrosion set up may be due, in the first instance, to differential aeration; the portion screened from oxygen by the débris becomes a small anode surrounded by a large cathode, but, when once corrosion product has accumulated, it may cause the attack to continue even after the original foreign body (which started the trouble) has been swept away. If the brass is of the "dezincing" type, "plugs" of copper may sometimes be formed which pass right through the tube walls, owing to the conversion of brass to copper. These may be inconspicuous, and the tube may appear unchanged, until tested with the knife, when the plugs are found to be quite soft. In some relatively acid waters, used in land plant, the copper may be deposited as a film over the brass surface—a much less dangerous development.

These troubles—which take many forms—can generally be prevented by keeping the tubes free from débris, using special brushes which do not scratch the tube (surface defects made by scratching might themselves be the starting points of attack). To prevent the attack (if it does occur) developing into dezincification, the brass should contain arsenic; antimony or phosphorus are sometimes used for the same purpose.

(2) *Impingement Attack* occurs most often when the water speed is *high*, as in many modern marine condensers. The complicated, turbulent flow of the water causes bubbles of low-pressure air to impinge on the tube surface near the inlet end of the tube. At points where *large* bubbles keep impinging on the tube, rapid pitting occurs; probably the film substance (which otherwise would be formed on the brass surface and would stifle attack) tends to cling to the bubbles as they leave the surface, and so becomes loose. Consequently stifling does not occur. In general the pits are free from corrosion product, and are undercut at the forward end; sometimes the deflection of bubbles by an adhering particle may lead to trenches of horse-shoe form.

Considerable advances towards the avoidance of impingement attack have been achieved by designing the condenser so as to prevent the impingement of large bubbles (small ones are harmless). The real solution, however, has come through the development of special alloys. These may be brasses containing aluminium, which give protective film (probably alumina) not easily damaged by impingement and capable o rapid self-repair if damage does occur; the composition favoured i 75–76% copper, 22–23% zinc and 2% aluminium. Another valuabl alloy consists of 70% copper and 30% nickel. Both give excellen resistance to impingement attack; the nickel alloy has the advantage o being free from any tendency to dezincification—since it contains no zin

Cavitation. Impingement attack in condenser tubes is closely allie to the cavitation which causes trouble on bronze ships' propellers water turbines and hydraulic and hydroelectric systems generally. I water flows rapidly through a locally constricted tube, it becomes milk at and beyond a certain point, owing to the formation of cavitie caused by the sudden change in flow conditions. They are often calle "vacuum bubbles", but must always contain water vapour, and usuall (if produced from air-saturated water) low-pressure air. Where the impinge on metal serious damage may be produced. This is ofte attributed to the "water-hammer action" caused by the blow delivere when a vacuum bubble "collapses" on coming into contact with a metalli surface. Undoubtedly mechanical damage due to such a cause can b severe, even in cases where corrosion is impossible; non-metallic substances, like bakelite, are affected, and metals can suffer cavitation damag in non-corrosive liquids like paraffin. Nevertheless, it seems probabl that the main damage caused in service by vacuum cavities is due t the protective film (which would otherwise stifle attack) being continuall sucked away, and, if this always happens at the same point (as is likel if the cavities always impinge at one place), the damage may be rapi and severe. The destruction is an example of *conjoint* mechanical chemical action; without the mechanical factors, the chemical change would soon become slow. (Cf. p. 126.)

The trouble cannot be overcome simply by selecting very har materials, nor, in general, by choosing alloys resistant to corrosion however, by combining good mechanical resistance with high chemica stability, lives can be considerably prolonged. Often it is still mor important to obtain a smooth surface with freedom from porosity on o just below the surface layer; this requirement suggests that the damag may be partly due to vapour cavities formed within such pores, which under rapidly fluctuating pressure, expand and contract, thus loosenin metal and protective films, and causing conjoint mechanical-chemica damage. But the main method advocated to-day for the avoidance o cavitation troubles depends on designing the shape of the moving part in such a way that any vacuum bubbles formed impinge at points wher they will do no harm; if this is impossible, a more resistant material, o a special surface condition, must be provided at points of impingement

Chapter V

EFFECT OF STRESS, STRAIN AND STRUCTURE

Structure of Metals and Alloys

General. The structure of metallic materials is especially important in connection with the influence of stress and strain on corrosion. In particular, the intergranular type of attack, which leads to far more damage than the total destruction of metal would seem to predict, is most often produced when stresses (applied or internal) act in a corrosive environment on alloys representing certain structures. Thus the three factors—stress, strain and structure—may conveniently be considered in a single chapter.

Cast Metal. When liquid metal is cooled below the melting-point, crystal nuclei arise at certain points, and from these nuclei crystals grow outwards until they meet one another, forming the grains of the ingot or casting; the orientation of the rows of atoms is different in different grains. If metal solidifies in a conducting mould (Fig. 50), the temperature drops most rapidly next to the walls, and nuclei (*a*, *b*, *c* . . .) appear there first. The resulting crystals will soon meet one another in the direction parallel to the walls, but can grow inwards for a long way before they meet others, so that the grains are elongated at right angles to the walls, forming the well-known *Columnar Structure.* If nuclei appear in the central region, where the temperature is more uniform, the crystals will grow out to a roughly equal extent in all directions before meeting their neighbours, and there will be no serious elongation in any particular direction; the effect is known as *Equiaxed Structure.*

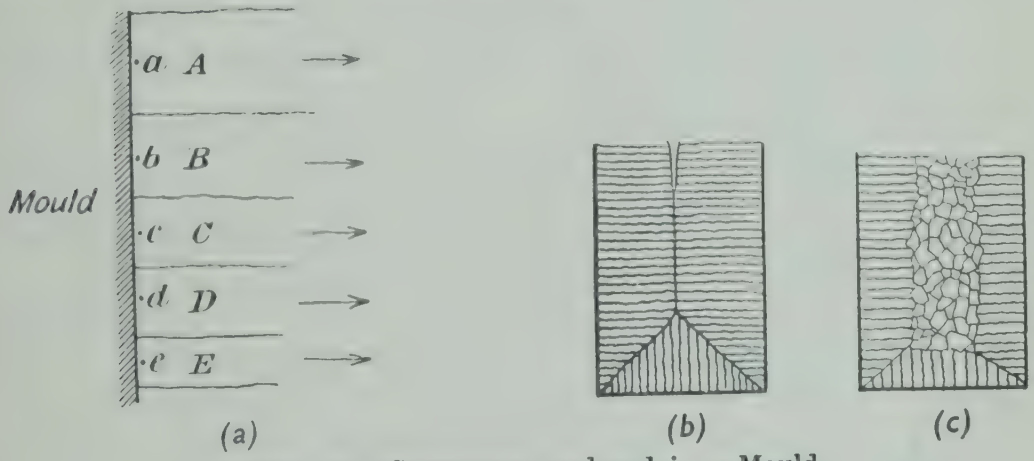

Fig. 50.—Structures produced in a Mould.

The form of the growing crystals (before they meet one another) will rarely be a simple geometrical shape. For instance, in metals whose atomic arrangement represents cubic symmetry, the growing grains will not be cubes, but dendritic or mossy growths, the spines or fronds of which represent the exaggerated prolongation of the cube diagonals. For growth in any direction will be restricted by the rate at which the heat of solidification can be removed; if a cube were to form momentarily, heat-removal would be greatest at its corners, which, losing heat with increasing ease as they grow outwards, will give rise to the dendritic form. The material between the dendrites will only become solid at a later stage.

If the liquid metal contains a small amount of a second metal, this will usually accumulate in the part remaining liquid to the last, so that the interdendritic matter will possess a different composition from the part forming the dendrites. On etching a prepared section with a suitable reagent, the dendrites will be shown up as a different colour from the interdendritic matter, explaining the " cored structure " often seen on sections of cast alloys. It may often happen that before the whole mass of a liquid alloy has solidified, the temperature has sunk below that at which the second metal (or a compound containing it) would separate out as a solid phase; in such cases, a eutectic structure appears, formed by alternate bands of the dominant metal and the second phase. Frequently metal to which no alloying constituent has been intentionally added develops traces of eutectic (due to impurities) between the grains.

Worked Metal. When cast metal is deformed by the application of stress, the change of shape largely consists in slices of metal gliding over one another, the gliding-planes being generally those crystallographic planes in which the atoms are most densely packed.

If the whole casting consisted of a single crystal, almost any change of shape could be produced by gliding along different series of gliding-planes, although the deformed mass would then present microscopic steps at the surface. In distorting a polycrystalline casting, the steps which would result from the simple gliding of neighbouring grains would not in general fit in with one another, and a more drastic disorganization of the crystal structure must be expected near the grain boundaries. This disorganization will require the performance of more work than ideal gliding, and, since the volume of material near the grain boundaries which undergoes disorganization will be greater on fine-grained than on coarse-grained metal, it follows that the work needed to deform metal will increase as the grain size diminishes; this explains why fine-grained metal is generally stronger and harder than coarse-grained metal.

Since deformed metal has portions where the original crystal structure is largely obliterated and others where the crystal planes, although still present, are bent or otherwise rendered imperfect, it is clear that gliding (the easiest mode of further deformation) will be less readily brought about on already deformed metal than on the original cast metal. This largely explains " work-hardening ", the enhanced hardness of " cold-worked " metal, i.e. metal deformed at a relatively low temperature; if the working (whether rolling, drawing or extrusion) is carried out at a higher temperature, so that the atoms can rearrange themselves as deformation proceeds, the extra hardness will not be acquired.

Annealed Metal. Metal which has been deformed, containing much disorganized matter, is in a higher state of energy than ideally crystalline metal, and will tend to return to the state of lower energy, if the atoms are sufficiently mobile for rearrangement. The number of nuclei formed in a given time will be greatest in the most highly deformed metal, since the amount of disorganized matter is greatest. Thus a highly deformed specimen heated rapidly to a given temperature will develop a larger number of new (undeformed) grains than a mildly deformed specimen heated to the same temperature; in other words, the greater the deformation, the finer the structure produced on annealing. The rate of heating is also important. If a mildly deformed specimen is heated very slowly, so that the first new crystal to appear grows outwards from its nucleus and embraces the whole specimen before a second nucleus has appeared at some other point in the disorganized matter, the whole specimen—even though it be a round bar or flat plate—becomes a single crystal, in the sense that the orientation of the atoms through the volume is the same; this is Carpenter and Elam's method of producing single-crystal specimens.

Certain other effects of casting and deformation are removed by annealing. The cored structure of alloys, due to the fact that the last-freezing portion is usually richer in one constituent than the early-freezing part, disappears on suitable annealing, which produces interdiffusion of the two species, until the composition becomes uniform. Another effect is the relaxation of internal stress left after deformation in the part where the crystalline structure—although not obliterated—has been modified, the atoms being brought unnaturally close in some directions and separated to an unnatural distance in others. Internal tension and compression often predominate in different parts of a deformed specimen. Heyn[77] showed that a cold-drawn bar is in longitudinal tension in its outer portions and in longitudinal compression in the centre. The internal tensional and compressional forces must be in equilibrium; if they were not, the rod would spontaneously change shape until equilibrium was reached. By gentle annealing, it is possible to allow the atoms so to accommodate themselves as to relax these internal stresses without permitting the drastic reorganization which would lead to the total loss of work-hardness. This is important, since certain dangerous forms of corrosion are bound up with internal stresses.

Effect of Structure on Distribution of Attack

General. Crystal structure may determine the incidence of corrosion in two ways:—

(*a*) When once an atom of a crystal has been dislodged, the work needed to dislodge others of the same (now incomplete) crystal layer is reduced, so that corrosion tends to produce facets determined by crystal orientation.

(*b*) Less work is needed to dislodge an atom at the boundary of two differently orientated crystals than to dislodge an atom in a crystal interior having all its neighbours similarly orientated; thus corrosion often starts at intergranular boundaries.

Production of Crystal Facets. Gwathmey and Benton [70] ground a single crystal of copper so as to form a sphere, and subjected it to anodic attack in phosphoric acid (using a hollow concentric sphere of larger radius as cathode). They found that the destruction of metal did not proceed uniformly (which would have left the spherical form unchanged, merely diminishing the radius), but occurred more slowly in some directions than in others; facets gradually appeared, so that the sphere became a polyhedron. The faces developed were those perpendicular to the direction in which corrosion is slowest; (in general, these represent crystal faces along which the atoms are densely packed and which therefore offer resistance to the attack). Glauner [66] made quantitative measurements of the corrosion velocity in different crystal directions on copper immersed (without current) in acids containing hydrogen peroxide; in acetic acid the corrosion was slower on the (110) face than on the (111) and (100), whereas in propionic acid the (110) face was the most rapidly attacked.

When a prepared section (such as is used for the microscopic examination of metals) is subjected to an etching agent, a system of little facets is produced on each grain; since the crystal orientation will vary from grain to grain, the inclination of the facets will also vary. If the section is examined under the microscope by vertical illumination, some grains will appear bright (those that chance to reflect light up the tube) and others dark (Fig. 51). On rotating the stage holding the specimens (or by changing the direction of light-incidence), the bright grains become dark and some of the dark grains bright.

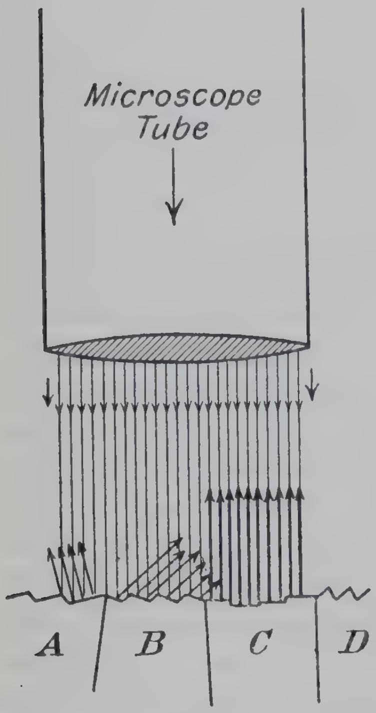

FIG. 51.—The Reason why some Grains in a Microsection appear Bright and others Dark.

Intergranular Trenches. On many specimens of metal, a second type of etching can be produced, resulting in the appearance of dark lines along the boundaries of the grains. These may arise in different ways. Sometimes two grains may be attacked to different depths, so that a difference of level arises, resulting in a shadow when the illumination is not vertical. On impure metal, the difference of composition between grain interiors and the borders often leads to a difference in corrosion-rate; if the boundary zones corrode the more slowly, they will constitute a network standing as relief, but if they are corroded preferentially, they will be engraved as trenches. Probably a common cause of special attack along the grain boundaries is the presence of small amounts of eutectic—

not always visible in microsections. A eutectic involves a large number of closely spaced grain boundaries and thus forms a zone of perceptible thickness, particularly susceptible to attack. Apart from this, the metal in a eutectic (or a eutectoid, the analogous structure formed from the solid state) is probably in a state of strain, the crystal-planes being bent, so that the material is especially susceptible to attack; the work of Whiteley and Hallimond [161] here deserves attention.

In unalloyed metal, the dark-boundary type of structure is difficult to develop unless impurities are present. For instance, on pure cadmium the grain boundaries are not easily shown up by etching, whereas cadmium containing a trace of zinc readily develops a network of lines marking the grain boundaries.

Factors determining the Crystallographic Effects developed during Corrosion. In their detailed study of the corrosion of zinc in potassium chloride solution, Bengough, Lee and Wormwell [8] observed that, when very pure metal was employed, crystal facets appeared; zinc crystallizes in the hexagonal system, and accordingly beautiful six-sided pits were cut into the grains. When small amounts of impurities were present, the attack was directed mainly on the grain boundaries, where impurities would be segregated, and geometrical figures were usually absent.

The facets developed by etching depend upon the corrosive agent. The six-sided pits developed on zinc placed in sodium hydroxide have sloping sides, representing pyramidal faces, whereas when hydrochloric acid is used, prism faces appear. Desch [27] has attributed the difference to the less dense atomic packing on the pyramidal planes which, although able to resist a weak corrosive like sodium hydroxide, fail to halt the advance of hydrochloric acid.

It is often the case that impure materials tend to be attacked—in the early stages—along the grain boundaries whilst pure ones develop crystal facets in the grain interiors; nevertheless, exceptions are known. Cases have been reported of intergranular attack on aluminium, magnesium or zinc of high purity. At first sight, it would seem that attack should commence at the grain boundary even on absolutely pure metal, since, as explained above, the atoms are here least firmly held. But in a perfect crystal, the layer of easily removable atoms along the grain boundaries is a very tenuous one, and it seems unlikely that, in general, corrosion will dig in deeply unless other favourable factors are present. If mechanical work or even cooling stresses have produced a disorganized zone along the grain boundaries, the strip susceptible to attack is likely to be wider, and intercrystalline corrosion may penetrate to a greater depth; possibly cases of intergranular attack in pure materials are attributable to such causes.

But even where the layers of susceptible matter separating the grains are relatively broad, several factors can retard the penetration of attack inwards from the surface along the grain boundaries. For instance, if the reaction requires the presence of a reagent (e.g. an acid) at the actual site of attack, the rate of renewal of that reagent at the bottom of a intergranular fissure must become continually slower as the fissure becom deeper. Even where the presence of the reagent is not necessary at th site of attack (e.g. if oxygen present at a cathodic area outside a fissu can provoke attack at the anodic area at the bottom of the fissure), th electrical resistance of the liquid path joining anode and cathode mu increase as the fissure deepens. If the metallic salts formed anodicall in the fissure interact with alkali formed cathodically to produce metall hydroxides just inside the mouth of the fissure, this may furthe increase the resistance. All these causes of obstruction will be lessene if tensional forces operate (due either to internal or applied stresse tending to open out the fissures, making them wider as they becom deeper. Hence stresses often favour intergranular attack—as pointe out below. The obstruction by hydroxides or basic salts will be lessene if the anodic and cathodic areas are widely separated, as in the intergranular attack on lead cable sheaths by stray currents discussed o p. 44.

Another factor militating against intergranular attack on relativel noble metals is the increase of the concentration of cations in the fissure which would shift the potential in the direction unfavourable to the continuance of anodic attack. The presence of substances which lock u the metal as complex ions will prevent this factor from coming into operation. Thus brass, which suffers general attack in most acids, undergoe intergranular cracking in ammoniacal atmospheres, provided that interna stresses are present; the ammonia probably locks up the copper as th complex ions $[Cu(NH_3)_4]^{\cdot\cdot}$, preventing the accumulation of $Cu^{\cdot\cdot}$ ions which would otherwise bring the action to a standstill. This is importan in causing the "season-cracking" of cold-worked cartridges stored in a atmosphere containing traces of ammonium carbonate, as is not unusua in India and other warm climates; (uncombined ammonia acts much more slowly, if at all). Season-cracking is mainly intergranular, but ca follow slip planes (indeed single crystals sometimes show the phenomenon). The trouble—once a serious problem—can be avoided by suitable annealing, so as to remove the internal stresses without destroying the work-hardness. The correct conditions were found by Moore and Beckinsale,[112] and the problem was discussed at length in a Symposium held in America in 1944.[135]

Another example is the crumbling of lead foil in an originally acid solution containing nitrate, which becomes reduced to nitrite. This is probably a true case of intergranular attack, due to penetration along the boundaries separating the grains, which fall apart from one another; single crystals of lead suffer no decay in the same solution. It is believed that the solution locks up the lead as complex nitrite anions, thus preventing the accumulation of $Pb^{\cdot\cdot}$ ions, and allowing the penetration to continue unchecked.

Anodic Polishing. When a mechanically polished section of metal is immersed in an etching agent or subjected to anodic attack, it usually becomes rough, owing to production of microscopic crystal facets, or to the corrosion of one phase in preference to another, or to penetration along grain boundaries. In special circumstances, the converse transformation is possible and a rough surface can be made smooth by suitable etching agents—or, more conveniently, by anodic action under carefully chosen conditions.

It was pointed out on p. 40 that to make an anode passive in moving liquid requires a higher current density than under conditions of stagnancy. It should be possible, therefore, to subject a rough surface to anodic action under such conditions of current density, that the depressions where conditions are stagnant remain passive whilst the excrescences are active, and thus to eat away the excrescences until the whole is plane. This is the basis of Anodic Polishing, introduced by Jacquet.[92] The solutions used vary with the metal; Jacquet recommends phosphoric acid for copper, whilst for aluminium, tin and lead he uses a mixture of perchloric acid and acetic anhydride.* For stainless steel two baths are advocated by different authorities; one contains glycerine and phosphoric acid and the other sulphuric acid, with an organic substance, such as citric acid. For some metals, very simple solutions can give good results; in the anodic polishing of zinc, Vernon and Stroud [154] use 25% potassium hydroxide, whilst for silver a bath similar to that used for plating but containing much less free cyanide will serve. The current density is held at a value not far from that at which active conditions pass into passivity; naturally, a higher value is needed for vertical than for horizontal surfaces.

An anodically polished surface is at least as bright as one mechanically polished, but is structurally different. In mechanical polishing, the metal is largely caused to "flow" in a soft, perhaps momentarily molten, condition, so that the surface becomes buried below a layer which is glassy and almost structureless. In anodic polishing, this glassy layer is absent, and the structure is probably crystalline up to the surface, which, however, usually remains covered with a film of the compound responsible for the passivity.

Stress Corrosion [135]

External (Applied) Stresses. Methods of carrying out corrosion tests on stressed specimens are shown diagrammatically in Fig. 52. In A, C and D the stressed specimen is immersed in the liquid, whilst in B the convex face can be kept wet with spray. In C and D, the total load applied will tend to fall off as the specimen begins to fail under corrosion cracking, but in A and B, the load will be maintained, and, since the cross-section of the specimen will diminish as the cracking extends across the test-piece, the stress (or load per unit area) will actually increase, so that cracking—once fairly started—will quickly lead to complete fracture.

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* For the anodic polishing of aluminium alloys, a bath containing aluminium chloride, zinc chloride, ethyl alcohol, and butyl alcohol has been used by D. Whitwham in the author's laboratory at Cambridge. This bath is also suitable for nickel and several other metals.

Internal (Residual) Stresses. In the cases just mentioned, a stres is applied externally. If a cold-worked article is immersed in a corrosiv medium, there will usually be present residual or internal stresses— tensional and compressional in different parts—in equilibrium. If, at a area in tension, corrosion sets in along grain boundaries, the stresse will keep opening out the grooves produced between the grains, whic should hinder blockage, and aid penetration. But the very yawnin will relieve the tensional stresses in the grains on each side of the crack and in this respect, internal stresses due to cold-work are less dangerou than externally applied stress. It must, however, be remembered tha cold-worked metal usually contains disorganized material, along the grai boundaries and on slip-bands, which will be rich in energy and probabl especially susceptible to attack.

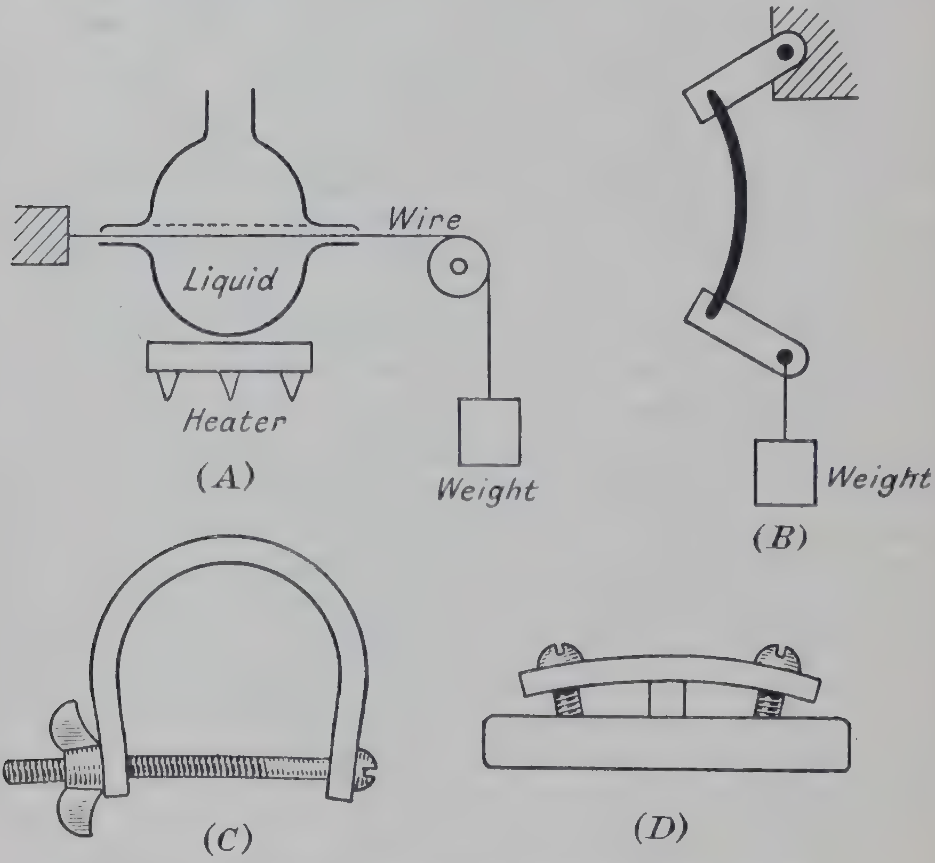

FIG. 52.—Methods of studying Corrosion under Stress.

Stresses set up by the Increased Volume of Corrosion Products Most solid compounds formed by corrosion occupy (if unconstrained) a larger volume than the metal destroyed in producing them. Rust, fo instance, normally occupies a larger volume than the iron contained i it. The formation of such a product within a cavity opening on to th metallic surface must set up a compressional stress, and will often hav one of two results: (*a*) it may seal the cavity and stop further attack within it, or (*b*) it may disrupt the metal. The decision between thes two contrary results depends upon the strength of the material, th eometrical relation of the cavity to the surface, and the existence of tresses, internal or applied, which may assist or oppose disruption.

Numerous cases are known where voluminous rust has developed orces strong enough to cause breakage. The snapping of rivets on ridges by rust formed in crevices between plates was mentioned on . 54, and the shattering of concrete by the corrosion of iron buried in t on p. 46 ; the pressures built up in such cases have been measured in he laboratory. Pipes at a sulphuric acid works are reported to ave burst through the expansion caused by iron salts formed within ores. Near acid works the author has found strips of iron swollen to everal times their original thickness. These had become quite rotten, but where, owing to external support, the swelling had been prevented, the internal attack had not taken place, evidently owing to sealing by the corrosion product. In such situations a bolt passing through the material may locally prevent swelling and disintegration. In the inspection of a marine structure, it was once noticed that the attachment of a ladder (not intended to give structural support) had arrested attack.

In rolled material, the grains tend to be elongated, the structure becomes pastry-like, and the majority of grain boundaries run parallel to the surface. Thus attack following the grain boundaries, which on a casting showing columnar (or even equiaxed) structure would soon stifle itself, can on rolled material follow a course just below the surface and parallel to it. The surface layers are forced up by the voluminous corrosion product formed below them, and this disrupts the material and prevents sealing. Aluminium alloys offer examples of this type of disintegration, but an analogous change has been observed on zinc (see Fig. 24 (D), p. 32).

Corrosion parallel to the surface is also met with on wrought iron and laminated steel exposed to the atmosphere, and is sometimes the cause of swelling—especially on railings near the coast. Cast iron and unlaminated steels are less liable to be disrupted by the internal pressures, because the grain boundaries do not systematically run parallel to the surface ; the forces are unlikely to be powerful enough to break up the metal, although they may expel liquid from pores. Cast iron which has remained in the sea for long periods, and is then taken out and dried, may appear unchanged. It usually contains, however, hygroscopic magnesium or ferrous chloride in pores, and after being kept indoors for a few days, exudes little globules of moisture, each covered with membranous rust. This phenomenon is sometimes useful as evidence that iron or steel has been exposed to sea water.

Similar drops may appear on objects which have been buried in salt ground ; they usually contain chlorides. Archæological treasures from salt deserts, brought to a museum, should be washed free from chloride, dried and placed in cases containing lime or caustic soda.

Intergranular Attack by Mercury, Tin or Solder. Interesting examples of the principles developed above are met with in studying attack by liquid metals or alloys. The atoms along a grain boundary, being in an energy-rich condition, will more readily combine with merc or molten tin than those of the grain interior, but the alloy formed usually occupy a larger volume than the "solid" metal required to p duce it. Thus, in absence of stresses, the penetration of liquid met along boundaries will be prevented by sealing. If, however, the sc metal is kept in tension by an applied force or by internal stress intergranular penetration may proceed.

For instance, cold-worked brass placed in mercurous nitrate soluti which precipitates metallic mercury, suffers intergranular disintegrati and cracking (especially if immersion in ordinary liquid mercury follow This forms the basis of certain tests for internal stresses in brass, a provides a means of ascertaining whether a brass article would be lik to develop "season-cracking" (p. 104) if exposed to warm damp containing traces of ammonium carbonate.

Brass or copper kept in tension and exposed to molten tin or sold is apt to suffer intergranular penetration, very small tensional for being sufficient; brass having straight intergranular boundaries is t most susceptible. Even steels are liable to penetration along the gra boundaries if kept in contact with molten solder whilst under longitudi stress; mild steel is less susceptible than high-carbon steel, whilst amo heat-treated alloy steels, the susceptibility increases with increasi hardness; cases of penetration of low nickel-chrome steel by soft sold have been reported on aircraft. Nickel, Monel metal and cupro-nick are less affected by solder than most other materials.

Effect of Internal Stresses on Corrosion by Aqueous Reagent Welded iron containers used for transporting mixtures of sulphuric a nitric acid sometimes undergo intergranular corrosion a few centimet from the weld-line, due to tensional stresses; annealing about 600° which removes the stresses, usually prevents this trouble. But, where tensional stresses promote attack, surface treatment of a kind calculat to close up fissures and leave the metal in compression parallel to t surface may sometimes increase resistance; the hammering of copp columns used in the distillation of acetic acid is said to lengthen the li

The employment of cold-worked zinc in making the tubes of electr torch batteries leads to more rapid perforation than occurs when anneal zinc is used; this may be due to an alteration in the distribution, rath than the total amount, of corrosion.

In some of the author's laboratory experiments,[36] bending has drasti ally altered the distribution, both on the compressional and tensional sid The total corrosion of iron partially immersed in potassium (or sodiu chloride (or sulphate) is usually determined by the uptake of oxygen the cathodic zone along the water-line; if the specimen is bent about vertical axis before being immersed, the oxygen supply is not likely be altered, but the corrosion is found to rise to a higher level along th bend axis than elsewhere.

Disturbance of the ideal distribution (p. 31) by bending may be due t cracking of the air-formed film, and film-rupture was certainly operativ n the author's experiments on copper in N/25 silver nitrate. Freshly braded copper, bent locally and at once immersed, showed general lackening, without any special phenomenon at the bend. Similar pecimens, kept nine days in a desiccator after abrasion, then bent and laced in silver nitrate, showed marked deposition of silver all round the end and little elsewhere. Specimens which were abraded, then at once ent and subsequently exposed to air for nine days before being tested n silver nitrate, showed no special deposition at the bend; the air-xposure had "healed" the damage.

Corrosion of Strained Metal in Acid Liquids. In acid liquids, vhere oxide films will usually be absent, it is the strain in the metal, not he damage to the film, which determines the distribution of attack. nteresting patterns are developed when locally deformed iron, after heat-ng at 200° C., is etched with acid cupric chloride (Fry's reagent). The nore rapid attack upon the strained metal is usually attributed to the energy stored up in the distorted material. Fry's reagent has been used in riminology to detect cases where identification numbers have been bliterated by thieves; the strain left by the punching remains even after he external form has gone, and application of the reagent shows up the igures once more.

In general, acid attacks cold-worked iron more rapidly than the annealed material; in contrast, straining makes little difference to the rate of attack by sea water, probably because the corrosion-velocity is here governed by the supply of oxygen, which will not be renewed more uickly on strained iron than on unstrained. The increased attack by dilute sulphuric acid on cold-drawn wire is probably connected with the higher energy content, but the enhanced corrosion of metal subjected to torsion may be partly due to the fact that torsion brings the segregate (including sulphides) to the surface.

Cold-working accelerates the action of hydrochloric acid on aluminium and magnesium, whilst annealing restores their resistance; the rate of attack upon tin, on the other hand, is often diminished by rolling, probably because tin recrystallizes spontaneously after rolling even at low temperatures, so that the lattice structure of tin may be more perfect after rolling than before it.

Intergranular Attack of Die-Casting Alloys. The zinc-aluminium alloys used in die-casting sometimes suffer intergranular attack—for instance in presence of steam. This appears to be due to traces of lead, tin or other metal. When rolled into sheet, these alloys tend to suffer exfoliation, probably due to the spreading out of impurities during deformation. Annealing at 300° C. for one day followed by slow cooling is said to confer resistance to steam at 95° C.

Nitrate Cracking. Iron wire surrounded by hot concentrated ammonium nitrate solution and subjected to tensile stress develops intergranular cracks; Smialowski [131] found that breakage may occur at 30% of the normal tensile strength. Other nitrates act in similar fashion, but less powerfully. Being oxidizing agents, nitrates stimulate the cathodic reaction, but for the same reason anodic action leads to passivity at m points, and attack is confined to the most susceptible zones, namely t grain boundaries. This may lead to a combination of a large cathode a relatively small anodic areas, with corrosion penetrating inwards alo the grain boundaries ; tensile stress is, however, needed for the propag tion, since otherwise the attack would stifle itself. Another condition needed for rapid breakage ; at ordinary temperatures the cathode (t free surface outside the cracks) progressively becomes covered up wi greenish slimy matter (probably hydrated magnetite, formed by int action between anodic and cathodic products), which, by preventing rap replenishment of nitrate at the true cathodic surface, slows down t change. At high temperatures the surface layer contains no water, b is a dark compact film, probably anhydrous magnetite, which bein conductor, can transmit electrons, so that the cathodic reaction can ta place on its outer surface. Thus it is found that nitrate cracking occu mainly at high temperatures, where the compact film is formed ; at low temperatures, where the slimy layer usually appears, cracking is le frequent.

Waber and his colleagues [159] attribute the intergranular character nitrate cracking to the presence of nitrogen in the steel, which, on agein undergoes a precipitation change so that the grain boundaries becor anodic to the rest of the material, possibly for reasons similar to tho which bring about the stress corrosion of light alloys. The " killing " steel with aluminium, which removes nitrogen, is held to impro resistance to nitrate cracking (and probably to the analogous caust cracking described below), whilst deoxidizers like silicon, manganese a vanadium, which do not remove nitrogen, confer little benefit. Crackin starts when the stress applied exceeds a threshold value ; on one ste ageing reduced this threshold value from 98% of the yield point to 73 or lower. Opinion differs, however, regarding the responsibility nitrogen for stress corrosion cracking in steel.

The danger of cracking in welded vessels handling nitrate solutio can be diminished by subjecting the steel to heat-treatment designed remove the internal stresses.

Caustic Cracking.[23] Dilute sodium hydroxide renders iron passiv but in hot concentrated alkali it becomes active again, dissolving wi liberation of hydrogen to give sodium *ferroate* or *hypoferrite* (Na_2FeO The behaviour of iron differs from zinc in that the passage from passi to active behaviour requires a higher alkali concentration, although th concentration needed diminishes as the temperature rises. Alkali ma give rise to serious cracking in boilers, especially in riveted boilers whe the riveting has been carried out too vigorously, leaving internal stress in the steel ; the cracks usually run from rivet hole to rivet hole, the ste between the cracks remaining ductile. In boilers the concentration sodium hydroxide in capillary crevices communicating with the outsic air is apt to rise through " evaporative leakage " (escape of steam throug crevices). If the concentration within crevices becomes so high as t render the iron active, whilst that at the surface of the plates or tubes remains low enough to maintain passivity, the usual combination of large cathode and small anode is set up, leading to serious attack, which may take an intergranular course if tensional stresses are present. Although good quality steel (especially if killed with aluminium) is less susceptible than poor material, the trouble cannot be avoided merely by selection of material.

To prevent cracking, it is important to avoid faulty alignment of the rivet holes, excessive riveting pressure and heavy caulking; in welded constructions, stresses should be minimized or relieved. The water should be adjusted to avoid the local formation of high concentrations of sodium hydroxide, sodium phosphate being used as conditioning agent (p. 140) in preference to sodium carbonate.

Some authorities recommend the addition of sodium sulphate, a salt whose solubility diminishes as the concentration of sodium hydroxide in water rises; it is believed that, at any place where the caustic soda concentration becomes excessive, sodium sulphate is precipitated as a solid, which may—in favourable circumstances—seal the crevices, and put a stop to the trouble. The remedy does not seem, however, to be infallible. On the other hand, sodium nitrate is largely used in locomotive boilers in the U.S.A. to prevent caustic cracking, apparently with good results. The fact that nitrates themselves can cause cracking when added to neutral water, producing just the border-line conditions between activity and passivity which lead to the dangerous combination of large cathode and small anode, is no argument against their beneficial effect in alkaline water, where that combination already exists, since here the addition of nitrate may lead to complete passivity. However, clearly each of these remedies, whilst useful under some conditions, may be inappropriate—or even dangerous—under others. The list of different substances advocated as remedies for caustic cracking is a long one; they include lignins and bark extracts. Quebracho has been helpful in stationary boilers, whilst waste sulphite liquors have reduced the trouble on American railways.

Hydrogen Cracking. It was explained on p. xxxiii how during cathodic polarization hydrogen may enter the metal in atomic form. Some metals, for example iron, will take up hydrogen at interstitial positions in the lattice. When hydrogen is electrolytically deposited on such metals, either by cathodic treatment in an appropriate electrolyte, or by the metal itself furnishing the concomitant anodic reaction, as in acid dissolution, it appears first in the atomic form; some of these atoms diffuse into the metal,* the remainder combining on the surface to give molecular hydrogen, which is evolved. If the diffusing hydrogen atoms reach an *internal* surface—i.e. a rift in the metal—they undergo similar combination and the molecular hydrogen produced gives rise to very high pressures, sufficient to cause blistering[33] if the rifts are not too deep.

If internal (tensional) stresses are present, e.g. on cold-worked steel, cracking and blistering may occur spontaneously during pickling in acid high-carbon steel articles are particularly apt to develop pickling cracks Sometimes these high internal pressures may be produced intentionall for a useful purpose; immersion in acids can be used to enlarge an show up cracks already present in metal but too small to be visible.

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* The hydrogen may pass inwards as protons *plus* electrons.

Hydrogen cracking is not peculiar to acid liquids. The action of ho concentrated sodium hydroxide on steel can lead to a type of intergranular cracking connected with the internal production of hydrogen this has been demonstrated by a group of investigators at the Nationa Physical Laboratory.[128] It is probably a different phenomenon from th caustic cracking commonly met with in boilers (p. 110), but opinion i divided as to how far hydrogen cracking contributes to the trouble arising in boilers under service conditions.

Hydrogen taken up at high temperatures may stimulate the formatio of hair-line cracks on certain alloy steels. The $\gamma \longrightarrow \alpha$ change, which o slowly cooled carbon steels occurs about 700° C., where the material i comparatively plastic, may, in the case of alloy steels, occur at a much lowe temperature, where the material is relatively brittle; unless care is taken cracking may occur. If hydrogen is present in the steel, it may mak matters worse in several ways. Being an austenite-stabilizer, hydroge may increase the amount of austenite retained after cooling. Whe finally this retained austenite changes to martensite, the hydrogen wil suddenly be evolved (being less soluble in α- than in γ-iron), and will thu produce high internal pressures, favourable to cracking.[86] Finally, th decarburization brought about by hydrogen will also promote breakdown. The glittering white fracture noted on hair-cracks (" snowflakes " is usually a sign of decarburization by hydrogen. Such white fracture are found in defects caused during the coating of iron with glassy enamel and also near welds; it is believed that hydrogen (whether taken up from a furnace atmosphere or during pickling) plays a part in causing such troubles, although the dangers attributed to it may have been overestimated in some quarters.

Intergranular Cracking in Stainless Steels. The austeniti variety of stainless steels (p. 86) contains chromium (often 18%), nicke (often 8%), with a small amount of carbon and other minor constituents In their most resistant state, they consist of a single austenitic (γ-iron phase. However, chromium has a high affinity for carbon, and if the alloy is heated, chromium carbide may separate out. This separation will occur preferentially at the grain boundaries, where the atoms, being least firmly held, are most mobile, and a network along the grain boundaries is left impoverished in chromium, the protective element Consequently austenitic stainless steel which has been heated to about 700° C., if exposed to a corrosive environment, suffers rapid attack along the intergranular network, which forms a relatively small anode with the rest of the grain as a large cathode. Certain reagents, notably acid copper sulphate, may eat in along the grain boundaries, until the grains fall out, and the whole solid mass of alloy becomes a powder, each particle representing a grain of the original metal; such a solution is used to test specimens for intergranular susceptibility.

Fortunately, the local impoverishment is only rapid over a temperature range around 700° C. At lower temperatures, the deposition of chromium carbide is slow, whilst at higher ones fresh chromium diffuses from the grain interiors to replenish what is lost near the boundaries.

Nevertheless the phenomenon causes trouble in service:—

(1) *in welding*, there is necessarily a narrow strip heated to about 700° C., on each side of the weld-line, so that the metal becomes susceptible to intergranular attack along these strips, even though the time of heating is short:

(2) any stainless steel part which becomes strongly heated for some time *in service*, even though the most dangerous temperature (700° C.) is not reached, may become susceptible to attack, the longer period compensating for the lower temperature.

Several methods are used for overcoming susceptibility to intergranular attack. The most obvious course, the elimination of carbon from the alloy, is difficult and seldom adopted. It is better to introduce an element which has an even higher affinity for carbon than has chromium. *Titanium* is considerably used, the amount introduced being four to six times the carbon content; it was once thought to remove carbon as TiC, but the compound is now believed to contain nitrogen as well as carbon. In recent years, *columbium* (*niobium*) has come into favour; the amount needed is larger, about ten times the carbon content, but it is less liable than titanium to be lost by oxidation.

Another method is to introduce an element which causes the appearance of α-iron in the alloy; tungsten, silicon or molybdenum have this effect. Probably the α-iron phase will be richest in chromium, and the γ-iron phase in carbon; if so, the chromium carbide will be precipitated near the edges of the α-iron masses, and *provided that these are disconnected*, no continuous paths of material impoverished in chromium (and therefore susceptible to attack) will be produced on heating in the dangerous range. It has also been suggested that chromium diffuses more rapidly through α-iron than through γ-iron, so that replenishment is more complete. Austenitic stainless steel intended for welding often contains tungsten as well as columbium or titanium; another variety is rich in silicon.

In many circumstances, these methods are effective, but in presence of certain chemicals, special corrosion near welds is still met with even where titanium and other elements are present in the material. It may sometimes be necessary after welding to heat to 1100° C. and quench in water so as to restore the resistant condition.

Stress Corrosion of Aluminium Alloys. Several of the light alloys used in aircraft, although resistant to corrosion in the homogeneous condition, become susceptible to intergranular attack after gentle heating, such as may be produced accidentally if aircraft are left exposed to powerful sunlight, or intentionally if the alloys have received "temper-hardening" treatment, or again if they have been coated with a stoving enamel (p. 155). If subsequently the alloys are exposed to a corrosi environment whilst subjected to tensile stress, they may lose strength a dangerous extent as a result of intergranular attack.

The causes are slightly different in the various classes of alloys. T alloys of aluminium with magnesium (often 8·5%) and mangane (perhaps 0·3%) throw down on heating the constituent Al_3Mg_2, whi is anodic towards the solid solution forming the main part of the allo Precipitation often occurs preferentially along the grain boundaries where the atomic mobility is greatest, as already explained—and, if continuous intergranular network were to be formed (leading to t usual dangerous combination of small anode and large cathode), inte granular attack under stress would be in no way surprising. Son German writers assert that intergranular attack (by acid) only occu where there is an Al_3Mg_2 network. This is possibly an over-simplificati of the facts, but it seems likely that the trouble—when experienced— mainly due to an unfortunate disposition of the phases. Many clain have been made to prevent susceptibility by adding other elements—suc as zinc or chromium—but it is doubtful whether success can be achieve on these lines. Interest may attach to a process based on heating in fuse nitrate the alloy with 8% magnesium; the surface layers lose magnesiu and become relatively resistant to corrosion.

Aluminium alloys containing copper frequently throw down along th grain boundaries $CuAl_2$ particles, which are strongly cathodic, leaving region impoverished in copper and anodic to the main portion of th alloy. If this anodic region forms an uninterrupted zone along th intergranular boundaries, the corrosion may produce a continuous trench if, through stress intensification, the attack is directed on to the *bottom* rather than the sides of the trench, intergranular cracking will resul This explanation of corrosion cracking was developed by Akimow Dix [29] reports that the P.D. at the grain boundaries is displaced by 0·04 volts in the anodic direction. Recent work by Whitwham at Cambridg affords general confirmation of Akimow's explanation, whilst suggestin the necessity of slight modification.*

These alloys are usually brought to an (approximately) one-phas condition by heating at a high temperature followed by quenching; the are then hardened either by heating to a lower temperature (temper hardening), or (in some cases) by storage at ordinary temperature— method less likely to cause trouble. Intergranular susceptibility ma arise if the quenching has been conducted from too low a temperature o in water insufficiently cold. The time interval between removal from th furnace and the actual quench should be made as short as possible. Slov quenching produces a precipitate which has been revealed microscopically whereas rapid quenching gives no precipitate and the susceptibility i absent. Rapid quenching in water, however, may leave internal stresses von Zeerleder [157] recommends quenching in oil.

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* The latest researches of Gayler at Teddington suggest that the copper-rich matte precipitated in the early stages, may not be $CuAl_2$, but this hardly affects the main principle of Akimow's interpretation of intergranular attack.

The susceptibility may also be caused by conditions of heating the quenched material. The dangerous temperatures vary with different alloys. *Duralumin*, containing 4% copper, 0·5% of magnesium, 0·5% manganese with small amounts of silicon and iron, was found by von Zeerleder to become susceptible after temper-hardening at 145° C.; in this condition it loses tensile strength and elongation quickly on subjection to salt-spray; (the alloy can be age-hardened at ordinary temperature, and such a course is preferable). *Superduralumin*, a similar alloy with 0·8% silicon, becomes highly susceptible after heating about 140° C., suffering a pock-form type of intergranular attack very prejudicial to tensile properties. *Lautal*, a magnesium-free alloy with 4·2% copper and 0·5% manganese, shows the greatest tendency to intergranular attack and weakening after heating at about 130° C.

Corrosion Fatigue

General. In the cases of stress corrosion hitherto discussed, the metal has been subjected to a *steady* stress (external or internal) and attack has usually been *intergranular*, since the grain boundaries constitute the zones where the atoms are least firmly held. In cases where the metal is subjected to *alternating* stress, energy-rich material is created continuously along the gliding-planes, and attack is *transgranular*, following, in general, those gliding-planes so situated that the resolved shear stress is maximal. Nevertheless, exceptions to this rule arise, and there are on record cases of transgranular corrosion cracking under conditions of steady stress, or of intergranular corrosion cracking brought about by alternating stress.

Dry Fatigue and Corrosion Fatigue. Even in the absence of corrosive influences, metallic specimens may ultimately fracture if subjected to alternating stresses well below the ultimate tensile stress. It is common knowledge that a piece of sheet or wire can be broken if repeatedly bent to and fro at a single point; rupture may also be produced if a rod is subjected in a machine to alternate pulling and pushing. The explanation usually offered for fatigue failure is based on the well-known fact that if an internal cavity, or a surface notch, is present in a rod subjected to tension, the stress (force per unit area) around the cavity or notch will be much greater than on the parts of the bar far away from the defect. Consequently, a rod subjected to alternating stresses too low to cause plastic deformation in the material as a whole, may nevertheless suffer gliding locally at surface defects where stress concentration occurs. At such points, work-hardened material will be produced, and after a time gliding will be prevented. If the stress range exceeds a certain value (the *fatigue limit*), the hardened material, unable to glide, will rupture, and the crack, once started, will produce further stress intensification, and thus propagate itself through the cross-section until fracture occurs. Below the fatigue limit, fracture will never occur—however long the alternating stress is continued—provided that corrosive influences are absent. But if they are present, the work-hardened material, being unstable, will be eaten away as it is formed, and the crack will extend however low the stress range.[71]

The effect of stress range on life (expressed on a logarithmic scale) i represented diagrammatically in Fig. 53, which shows how, under dr fatigue conditions, there is a limit below which the life is infinite, wherea with corrosive influences present, there is no such limit. Thus in fatigu tests carried out in a corrosive environment, it is merely possible to ascertain the stress range below which the specimen will endure a specifie number of cycles without fracture; this is known as the *endurance limit* The endurance limits of various materials in air, fresh and salt water—based on the extensive measurements of McAdam [101]—are collected i Table XIV. It will be noticed that even in air, the limit is far below th ultimate strength, and that for most materials the number obtained from a test conducted in water is far lower still. The sole exception is coppe

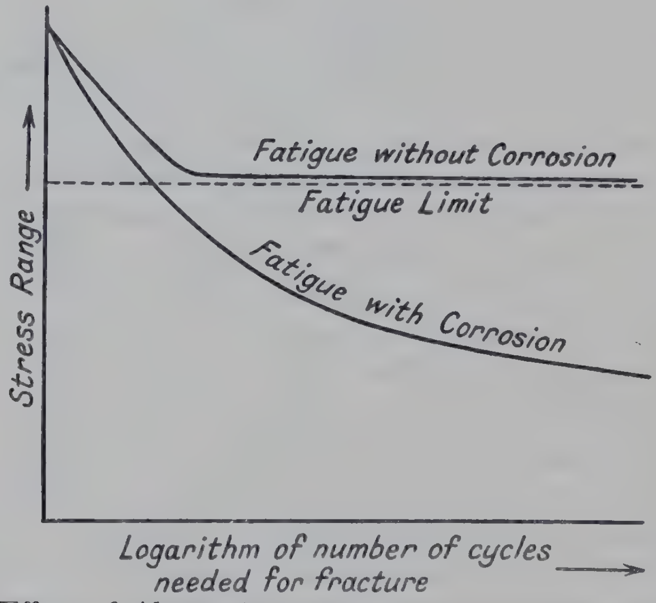


FIG. 53.—Effect of Alternating Stresses with and without Corrosion.

where corrosion has produced no lowering; indeed, probably owing to its cooling action, the fresh water has actually raised the endurance limit.

Even in so-called dry fatigue tests with no corrosive influence intentionally introduced, the endurance limit number can be appreciably increased by carefully greasing the specimen, or by carrying out the test in an atmosphere of a dry, neutral gas free from oxygen—as indicated by Gough and Sopwith; [67] possibly the exclusion of water vapour is as important as the exclusion of oxygen.

Methods of Measuring Resistance to Fatigue and Corrosion Fatigue. Alternating stresses can be applied in several ways. Rod specimens may be alternately stretched and compressed in a push-pull machine, conveniently worked by an electromagnet; alternatively they can be subjected to torsion, being twisted first in one direction and then in the other. A commoner procedure is to use a horizontal rotating rod, carrying a weight at one or more places which has the effect of bringing each point on the surface alternately into tension and compression ; in a convenient form of rotating bar test shown in Fig. 54, the weight is supported at two points, so that the load is constant over the length between the points of support. For if the weight applied at each point is W, and the distance between them is L, the effect at a distance x from the left-hand support will be $Wx + W(L - x) = WL$, and is thus the same, whatever the value of x.

TABLE XIV

Effect of Corrosion on Fatigue-Strength (S. F. Dorey, based on D. J. McAdam)

Material	Ultimate Tensile Strength. Tons per sq. in.	Endurance Limit ± Tons per sq. in. Approximately 5 × 10^7 cycles		
		Air	Fresh Water	Salt Water
0·16% Carbon Steel (hardened and tempered)	29·3	16·0	8·9	4·0
0·24% Carbon Steel	24·8	10·3	7·6	—
Copper Steel (0·98 Cu, 0·14 C)	27·5	14·3	8·9	3·5
1·09% Carbon Steel	46·2	17·85	9·4	—
Ni Steel (3·7 Ni, 0·26 Cr, 0·28 C)	40·5	22·0	10·1	7·1
Cr-V Steel (0·88 Cr, 0·14 V)	67·2	30·0	8·0	—
Ni-Cr Steel (1·5 Ni, 0·73 Cr, 0·28 C)	62·0	30·3	7·2	6·2
Stainless Iron (12·9 Cr, 0·11 C)	40·0	24·5	17·0	13·0
Stainless Steel (14·5 Cr, 0·23 Ni, 0·38 C)	42·0	23·2	16·0	16·0
Ni-Si Steel (3·1 Ni, 1·6 Si, 0·5 C)	112·0	48·7	7·5	—
Monel Metal (fully annealed)	36·5	16·0	11·6	12·5
Pure Nickel	34·0	14·8	10·4	—
Nickel (cold-rolled)	58·7	22·3	13·0	10·7
Duralumin	31·0	7·8	4·5	3·6
Aluminium Bronze (7·5 Al)	40·2	14·5	11·2	9·8
Pure Copper (annealed)	13·6	4·2	4·5	—

Notes. The " Fresh Water " was a well-water containing calcium carbonate. The " Salt Water " was a river-water with a salinity about one-sixth that of sea-water. Speed of tests = 1450 cycles per min.

For testing a wire specimen, it may be kept bent into a bow form and then rotated, so that each point is alternately stretched and compressed. In the Haigh-Robertson fatigue machine, used at Cambridge, the wire is bowed in a horizontal plane ; in the Kenyon machine, which has been adapted for corrosion fatigue by Fink, Turner and Paul,[58] the plane is vertical and, the bending forces being applied at four points, a uniform stress is maintained over a length of wire, for the reason just explained.

In most of the testing methods indicated above, the stress fluctuates about zero stress as the mean value. In service, it may sometimes fluctuate about a mean which is not zero ; probably the severest condition will generally be those where the mean value is tensional.

Nearly all the machines hitherto described were originally designed a pure fatigue machines but have been adapted for corrosion fatigue testin

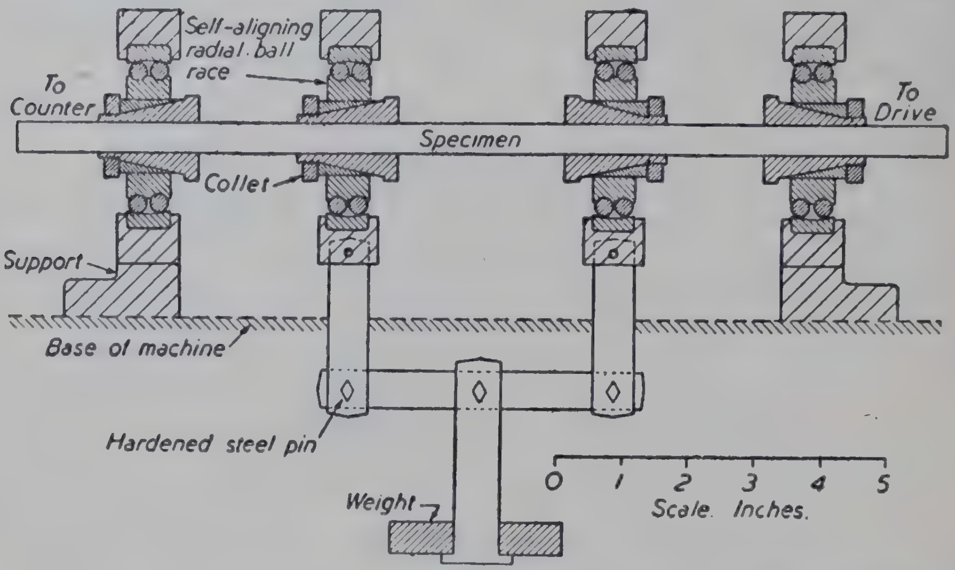

Self-aligning radial ball race
To Counter
To Drive
Specimen
Collet
Support
Base of machine
Hardened steel pin
Weight
0 1 2 3 4 5
Scale. Inches.

FIG. 54.—Fatigue-testing Machine giving Uniform Stress between the Two Loading Points.

by directing salt spray or a stream of water on the specimen, or even (as in the Kenyon machine) by arranging the lower part of the bent wire to rotate below the surface of the corrosive liquid. There are certain special features called for in a reliable corrosion fatigue machine which the dry

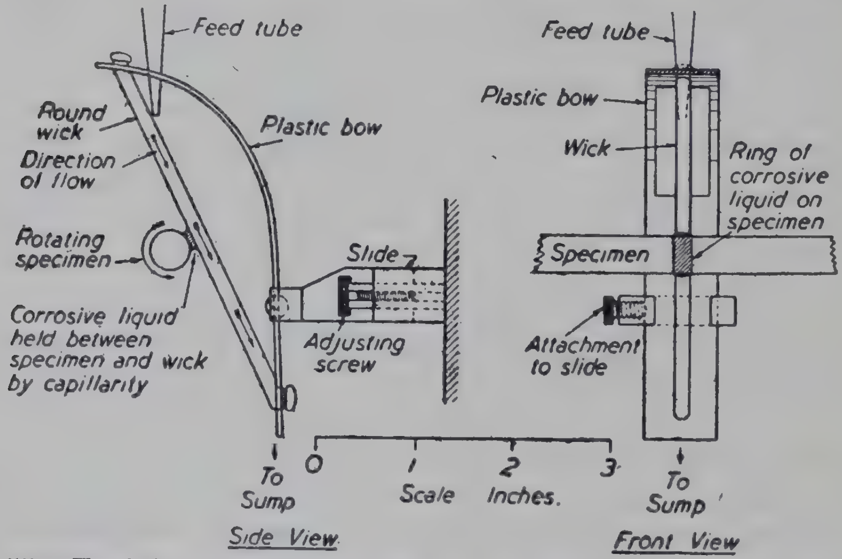

Feed tube
Round wick
Direction of flow
Plastic bow
Rotating specimen
Slide
Corrosive liquid held between specimen and wick by capillarity
Adjusting screw
To Sump
0 1 2 3
Scale Inches.
Side View
Feed tube
Plastic bow
Wick
Ring of corrosive liquid on specimen
Specimen
Attachment to slide
To Sump
Front View

FIG. 55.—Feed for Corrosive Liquid (A. U. Huddle and U. R. Evans).

fatigue machine does not provide ; one is that the machine itself shall be built of relatively corrosion-resisting material ; Huddle has designed a machine for use at Cambridge in which duralumin replaces steel. He has also designed [87] a special method of feeding corrosive liquid on to a rotating rod specimen (Fig. 55). The liquid runs down a wick, held taut n a curved plastic bow attached to a slide, which, by means of a screw, can be made to approach the surface of the rod until the distance is such that a film of liquid is held between wick and rod ; the rotation carries a narrow ring of liquid right round the periphery, and this is constantly renewed, thus providing a well-defined and reproducible wetted area without any contact between metal and wick. Tchorabdji-Simnad,[140] also at Cambridge, has adopted the principle for his work on wires stressed in the Haigh-Robertson machine, but, in place of a wick, he runs the liquid down a glass rod coated with wax except for a pathway on the side nearest the wire ; the liquid follows this unwaxed pathway.

Procedures for Corrosion Fatigue Tests. Two main procedures are available :—

One-Stage Tests. Here the corrosion fatigue is *continued until breakage.* The logarithm of the number of cycles needed to produce breakage is generally plotted against the stress range, as in the curves of Fig. 56, selected by Gough from McAdam's experimental data.

The effect of *Frequency* deserves attention, since, in order to obtain quick results, laboratory tests are commonly carried out at frequencies much higher than those normally met with under service conditions. But although the time needed to produce fracture, measured in hours, is shortened by testing at high frequency, the number of cycles needed to produce fracture is increased thereby, since the damage done by corrosion during each cycle is diminished if that cycle is short. Thus the low-frequency stressing which occurs in service may be regarded as either more destructive or less destructive than the high-frequency stressing adopted in the testing-room, according as duration is expressed in number of cycles or in days and hours.

Two-Stage Tests. Here the corrosion fatigue is interrupted after a definite number of cycles, and the residual strength is estimated by measuring either (*a*) the endurance limit in the absence of corrosive influences, (*b*) the number of cycles needed to produce fracture in the absence of corrosive influences, (*c*) the tensile strength, or (*d*) the shock resistance (Izod number). Of these four criteria of residual strength, chosen to measure the damage suffered in the first stage, (*a*) was used by McAdam, (*a*) and (*c*) by Gould, (*b*) by Tchorabdji-Simnad, (*c*) and (*d*) by Huddle.

Simnad's results [140] are especially interesting. He subjected steel wire wetted with potassium chloride solution to alternating stresses for different periods, then dried the wire and subjected it to alternating stresses in the absence of corrosive agency until fracture occurred ; it made little difference whether—in the second stage—the wire was surrounded by air or by a solution of potassium chromate, an inhibitor of corrosion. Since the stress range used was below the air fatigue limit, the life was infinite when the first (corrosion) stage was zero, but the total life (both stages) became very short when a comparatively short

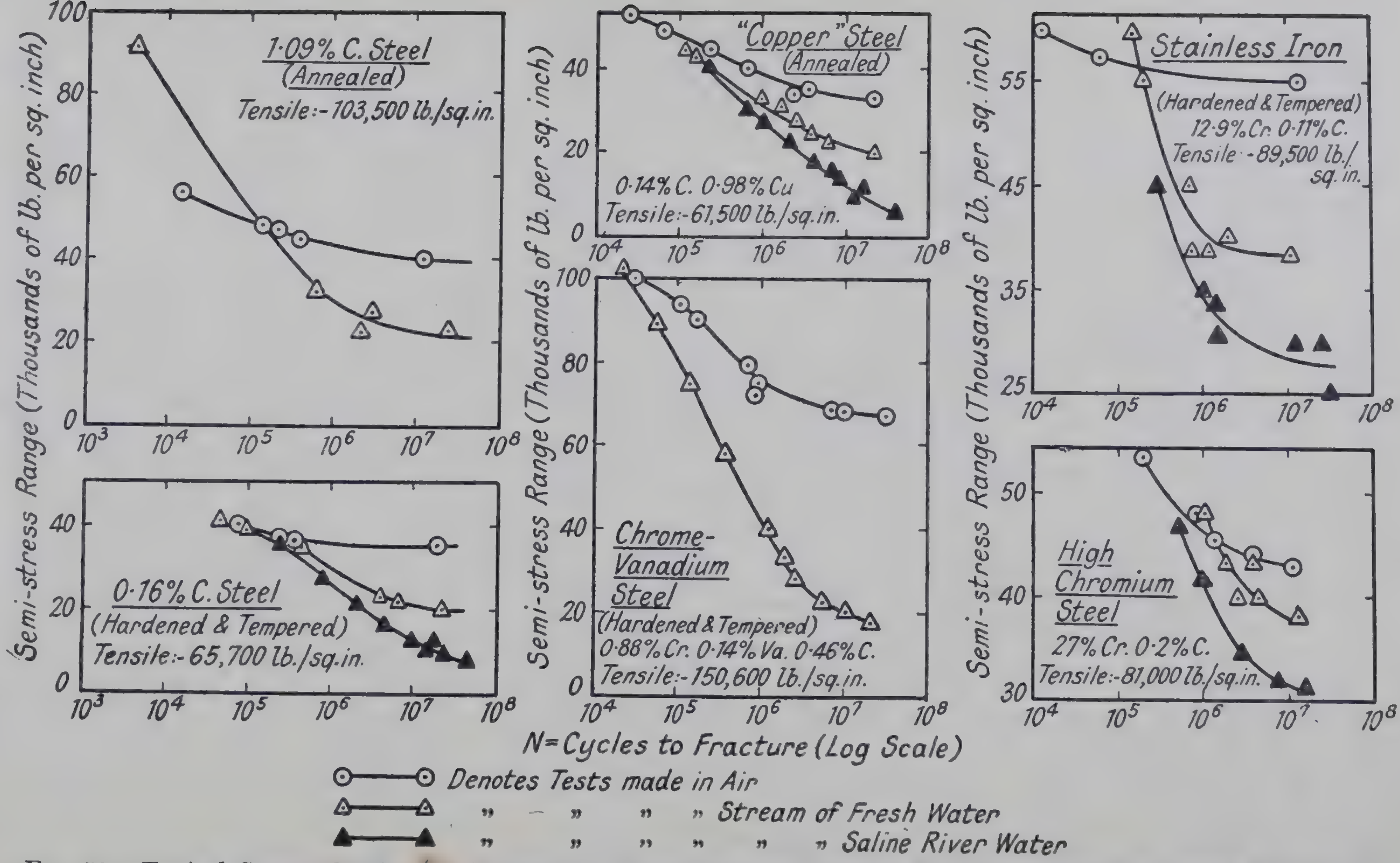


Fig. 56.—Typical Curves showing the Number of Cycles needed to Produce Fracture at Different Stress Ranges in Absence and Presence of Corrosion (H. J. Gough, based on data by D. J. McAdam).

period of corrosion was allowed. Curiously, if the corrosion period was prolonged further, the total life became longer again.

Simnad has provided an explanation based on Stress Concentration. At the outset corrosion produces a number of roughly hemispherical pits on the surface. If one of these (through some local peculiarity) happens to be slightly more pointed at the bottom than its neighbours, the stress intensification will be greater at the bottom of this particular pit than at the bottom of the others ; since stress, by distorting the lattice or rupturing protective films, will render the iron anodic, the E.M.F. working between the bottom of this pit and the aerated cathode outside will be greater than that operating at other pits. Thus corrosion will be stimulated at its bottom, making it still more pointed and raising the E.M.F. further. Consequently, having once started, this particular pit will develop downwards as a crack. At first sight it might seem likely that the pit in question would propagate itself right through the metal. However, when the crack becomes very sharp, the increase in resistance as the crack deepens will outweigh any further rise in E.M.F. Sooner or later, therefore, the rate of propagation of this first crack will slow down, and other pits will begin to develop into cracks. If the corrosion stage ceases when only isolated pits have developed into cracks, the concentration of stress at the tips of the cracks will be very high, so that if the alternating stresses are continued under dry conditions, without further application of corrosive substance, failure will soon occur. If corrosion continues until there are numerous cracks close together, the stress concentration is less, and the rate of propagation of the cracks under dry conditions is slower. Consequently the total life up to fracture is longer when corrosion is continued to failure than when it is discontinued at the stage of high stress concentration.

Simnad's experiments are important, not only in revealing the probable mechanism of corrosion fatigue, but in suggesting that, in service, protective measures, if they are to be effective, must be continuous ; if the precautions taken to exclude corrosive influences are relaxed even for a short period, the life of the member affected by corrosion fatigue may actually be shorter than if no protective measures had been applied at all.

There is no doubt that corrosion fatigue failures are due to sharp cracks. McAdam and Geil's photographs [103] show clearly the contrast between the hemispherical pits formed under stressless corrosion and the elongated fissures produced when alternating stresses are present in addition to corrosive influences.

Corrosion Fatigue Failures in Service. Breakdowns due to corrosion fatigue have become increasingly common in engineering practice during recent years when the introduction of new materials with enhanced tensile strengths (and even high fatigue limits as judged from tests in air) has appeared to justify reduction in dimensions ; if these reductions are made without consideration of the possibility of corrosion fatigue, serious trouble may be expected.

The earliest example of corrosion fatigue was the failure of paravan towing ropes, during the war of 1914–18, which Haigh rightly attribute to the chemical action of the aerated salt water acting on the vibratin wires. Since that time, numerous examples of premature failure du to corrosion fatigue have been reported from ships (propeller shaft rudders and dredger pins), aircraft (especially flying wires), railway (axles exposed to dripping from carriages, also steel sleepers), pump (shafts, rods and bodies), boilers (tubes and superheaters), rock dril (at the central hole through which water is forced to wash out debris automobiles (steering arms and axles) and even pedal cycles, where th familiar breaking of spokes has been ascribed by Huddle to corrosio fatigue.

Prevention by Choice of Materials. Although some of the ne “ strong ” alloys exhibit poor resistance to corrosion fatigue, materia exist which combine resistance to corrosion fatigue with good mechanic strength. The austenitic stainless steels, which show excellent resistanc to stressless corrosion, behave well even in presence of alternating stresse

The numerous measurements of corrosion fatigue on different materia made by McAdam and others[101]—of which a few are collected i Table XIV (p. 117)—may be helpful in guiding choice of materials, bu other factors should be borne in mind in predicting liability both to pu fatigue and corrosion fatigue. On certain materials, the presence notches (whether produced intentionally, as part of a design, or unintentionally as the result of a rough surface finish) will gravely prejudic performance, as a result of stress concentration; other materials, lik grey cast iron (where fissures exist following graphite flakes) are alread “ notch-saturated ”, and the addition of further notches has little effec Again, if a member of a machine or structure is exposed to vibration at frequency close to its “ natural period ”, resonance may set up oscillatio of increasing amplitude which are very likely to cause failure, unless th material is one of high “ damping capacity ”, which will dissipate th energy as heat and prevent dangerous amplitudes being reached. Stainless iron (p. 86), which has good corrosion fatigue endurance, is als outstanding in its damping capacity.

Importance of Design in Avoiding Fatigue Breakdowns. Quit as important as correct choice of materials is the careful design of machin and structures so as to avoid stress concentration. In marine practic fatigue failure has been known to start from places where the stress ha been raised locally owing to the faulty shape of some stressed member in different cases, stress concentration has originated in an oil hole, in small shoulder, in marks left by tools, or in unsuitable surface conditio generally; small flaws or grooves must be scrupulously avoided. Pi or notches left by previous corrosion (produced in absence of stress) a also known to have been starting places of trouble, and laboratory test by McAdam and Clyne[102] show that these can cause considerable loss fatigue strength.

Prevention by Peening. Whilst microscopic notches in the surfac layers and tensional stresses, which help to keep them open, tend to promote fatigue and corrosion fatigue, internal stresses which represent a compression in the surface plane have the opposite effect. Early experiments at Brunswick proved that steel specimens previously subjected to treatment in a special machine designed to leave the surface in compression enhanced fatigue-resistance. It may be doubted whether mechanical pretreatment will have wide application, and in practice compressional stresses are usually applied by peening, that is bombardment with round shot. Under correct conditions, peening confers enhanced resistance to fatigue and corrosion fatigue ; bombardment with jagged shot, which may leave grooves, is much less desirable. Recent work by Gould at Cambridge suggests that peening may greatly prolong the corrosion fatigue life of steel in contact with very dilute acid ; the best results are obtained with rather large round shot.

Prevention by Nitriding. Similar benefits may be brought about on ferrous materials by producing in the surface layers certain nitrides which are not only very hard but voluminous. Special steels are employed containing elements like chromium and molybdenum possessing an affinity for nitrogen ; aluminium and vanadium are often present. Some of these materials have a high pure fatigue strength even before nitriding, but their resistance to corrosion fatigue is enormously enhanced by heating in anhydrous ammonia. The effect is ascribed to the volume increase accompanying the formation of the nitrides, which produces a state of compression in the surface layers. The process has been called "Chemical Peening". The improvement is illustrated by the figures of Inglis and Lake [91] reproduced in Table XV, which also brings out the good performance of austenitic steels.

Prevention by Metallic Coats. Alternating stresses are likely to accentuate any discontinuity in a coating, and it is not surprising to find that coatings of metals cathodic to steel—like nickel or copper—do not generally prevent corrosion fatigue failure, and may even stimulate it. Nickel deposits are particularly bad when they carry internal stresses, since any cracking which starts in the coat may extend down into the steel, although this can be prevented if a coating of lead is applied below the nickel. On the other hand, zinc, which is anodic, serves to prevent or delay corrosion fatigue failure in steel, even if the coat is discontinuous. It is best applied by electrodeposition or spraying. Coats obtained by dipping steel in molten zinc tend to prevent corrosion, but the formation of a brittle alloy layer at the base of the coat may be a starting point of fatigue cracks, so that results are variable. In Gould's laboratory experiments,[68] mere winding with zinc tape, leaving the steel exposed to salt water between the turns, increased corrosion fatigue life, but this plan is probably not suited for typical service conditions. Spraying with aluminium is said to have given good results when followed by enamel, but cadmium coats show a rather variable performance ; one authority attributes the disappointing results sometimes obtained to hydrogen in the steel.

TABLE XV

Effect of Nitriding and Other Factors on Fatigue
(N. P. Inglis and G. F. Lake)

Material	Fatigue Limit (Air). Tons/sq. in.	Corrosion-Fatigue Limit (Tees Water), Tons/sq. in.
Mild Steel	± 17·0	± 2
Mild Steel, nickel plated	± 11·2	not more than ± 3
Nitralloy Steel (1·58% Cr, 0·87% Al, 0·33% Mo, 0·26% carbon)	± 33·0	± 5·0
Nitralloy Steel, nitrided	± 37·0	± 25·0
18/8/1 Cr/Ni/W Steel, fully softened	± 17·6	± 11·1
18/8/1 Cr/Ni/W Steel, air-cooled from 650° C.	± 17·6	± 6·5

Prevention by Organic Coats. Steel and light alloys are frequentl treated with paints or enamels for the prevention of corrosion fatigue the light alloys should first receive chemical or electrochemical treatmen (e.g. anodizing). The best results seem to be given by paints containin synthetic resins or rubber; in Huddle's tests on steel,[87] polystyren richly pigmented with metallic zinc (p. 159) has prolonged the corrosio fatigue life; this gives cathodic protection even in cases where the reager has access to the steel, but further work will be needed before the efficier prevention of corrosion fatigue by painting can be regarded as assurec

Prevention by Water-Treatment. For preventing the corrosio of the piston rods of oil engines by the cooling-water, Dorey [30] has successfully used emulsifying oils (p. 137). Chromates have been employed i other cases; in laboratory tests by Fink, Turner and Paul,[58] zinc yello ($4ZnO.K_2O.4CrO_3.3H_2O$) was shown to be more effective than potassiu chromate, owing to the favourable influence of the zinc ions. Gould studied the effect of chromates on the corrosion fatigue of wires subjecte to alternating stresses in chloride solution. He measured separatel (*a*) the time at which the protective film broke down (as shown by sudden drop of potential) (*b*) the (longer) time needed to break the wir Both film-life and wire-life were shortened as the chloride concentratio or stress range was increased; rise in chromate concentration lengthene the lives up to a certain value, but they never became infinite.

Wear

Dry Friction. The extensive work of Bowden and his colleagues has shown that when two unlubricated metal surfaces move relatively t one another, the motion is often jerky and consists of alternate *slippin* and *sticking*. During periods of slip much heat is evolved, and th temperature may in some circumstances approach or reach the melting point, when the surfaces stick together and movement ceases until th force accumulated bursts the bridge and a slip once more occurs. Friction is less when both surfaces are composed of different materials than if they are formed of the same material—as is easily understood—but it is, in the latter case, diminished if the material consists of two phases; thus ordinary steel causes less friction than austenitic steel. The presence of a film of oxide, sulphide, chloride or iodide will diminish the risk of welding, and thus reduce friction; consequently metal carefully cleaned *in vacuo* furnishes unusually high friction numbers, which diminish as soon as a trace of oxygen gains access to the metal. In a properly lubricated bearing surface, seizing should not occur, but other troubles may sometimes be encountered:—

Corrosion by Lubricants. If a lubricating oil contains fatty acids, it may be corrosive at the outset, but much of the corrosion suffered by bearing surfaces is probably due to acids formed by oxidation during service; certain metals, notably copper, catalyse the oxidation. Sulphur in oils may act in different ways, as shown by Beeck; [7] in his experiments, sulphurized sperm oil gave a thin, protective film, whereas sulphurized cotton-seed oil gave a coating which was too thick to protect, breaking up readily under severe conditions. Beeck also showed that if a crank case is well vented, permitting volatile bodies to escape from the oil, corrosion is far less severe than if they condense and flow back.

Corrosion in Internal Combustion Engines.[31] The wear of the liners of internal combustion engines is often regarded as purely mechanical wastage, but if this were the case, the rings and liners, if made of the same material, should wear away equally, whereas in practice the liners waste far more rapidly. It seems that the trouble is due to products formed by combustion of the fuel (which include not only water, but also nitric, sulphuric and carbonic acids) condensing on the relatively cold walls. This may occur for a short period just after the engine has been started, before the walls have warmed up; the advice sometimes given to allow the engine to " tick over " and warm up gradually would seem, from the corrosion standpoint, to be unsound. It appears likely that corrosion may also be caused by condensation occurring after the engine has ceased to run and is beginning to cool down; substances condensing in the evening may have the whole night to act on the steel; if further research should show that this is an important cause of wastage, it might be beneficial to provide means for flushing out the cylinders with dry air at the end of the day's last run.

Frettage. Whilst, at bearings where relative motion is desired, wear can be largely avoided by suitable lubrication, a different type of damage occurs at places where slight slipping occurs between two steel surfaces which are *intended* to be firmly clamped together. If the small relative movement is within the range of elastic distortion, no change in the material is produced; but beyond this the movement produces a debris, often known, from its appearance, as *cocoa*. Hard materials are more affected than soft ones, which seize easily, so that the undesired sliding does not occur; if it is impossible to prevent the movement by increasing the pressure between the surfaces, the interposition of soft materia between the two hard surfaces may solve the problem ; or V-serration may be substituted for flat faces. The seizure-pitting of gudgeon pin of pistons, which even if tight when cold may become loose when ho permitting slight relative motion to occur, is said to be largely prevente by a thin coat of aluminium paint.

The product of this type of wastage is essentially oxide. On stationary surface exposed to air, oxidation will, of course, be retarde as the film thickens and will soon, at ordinary temperatures, becom negligibly slow. Where there is relative motion, the temperature wi be raised by friction and the film may be rubbed off periodically, thu exposing fresh metal, so that the retardation will never be realized and th mean rate of destruction may be serious. The fact that interferenc colours have been noticed on such surfaces supports this cause of th wastage. If, however, the trouble were solely due to oxidation, wastag would cease if oxygen were completely excluded. Many attempts hav been made to test experimentally whether frettage ceases in the absenc of oxygen, and different experimenters, working under different conditions have obtained contradictory results. There does appear to be les destruction when oxygen and moisture are both excluded, and th products are different according as one or both are present ; but it is no improbable that, even in completely dry, anaerobic conditions, alternat slipping and sticking would cause damage to the metal if the pressure wa sufficiently high, and since the metallic debris formed would combin with oxygen as soon as it was collected and brought into air for examination, the final product would be oxide in this case also.

CHAPTER VI

PREVENTION OF CORROSION BY SOLUBLE INHIBITORS

Principles of Inhibition [134]

Cases where Electrochemical Action will lead to Stifling. It was explained on p. 27 that electrochemical corrosion is dangerous mainly because it frequently leads to soluble bodies as the immediate cathodic and anodic products, so that the reaction is not stifled. If, however, the electrolyte is one producing a sparingly soluble compound at either anode or cathode, stifling usually occurs and corrosion is checked.

The author's early experiments [35] on drops of salt solutions placed upon a horizontal steel surface showed that whilst drops of potassium sulphate (or chloride) caused much corrosion, similar drops of zinc sulphate solution produced less attack than the distilled water used in making up the solution. Drops of sodium phosphate mostly left the steel unchanged in appearance, only a trace of iron compound being found in the liquid; in those (exceptional) drops where visible corrosion did develop, the attack by sodium phosphate was considerable.

The absence of serious attack by zinc sulphate and sodium phosphate in normal cases is connected with the low solubility of zinc hydroxide (the cathodic product) or of iron phosphate (the anodic product). Zinc sulphate drops produce on the iron a clinging greyish-buff deposit, apparently zinc hydroxide coloured with some compound containing iron (probably a hydrated spinel $ZnO.Fe_2O_3.nH_2O$), formed by action of ferrous sulphate (the anodic product) on zinc hydroxide (the cathodic product). Sodium phosphate drops, where they cause any visible corrosion at all, produce it at the edges of the drop; the cause of this special corrosion at the meeting place of solution, metal and air is discussed on p. 135.

Zinc sulphate may be termed a *cathodic inhibitor* and sodium phosphate an *anodic inhibitor*, since they stifle the cathodic and anodic reactions respectively. Sodium carbonate and bicarbonate can both act as anodic inhibitors, if present in sufficient concentrations, probably because the solubilities of ferrous carbonate and/or bicarbonate are depressed by excess of $(CO_3)''$ or $(HCO_3)'$ ions. In the drop experiments just mentioned, whenever N/10 sodium carbonate produced any visible attack at all, this exceeded the amount arising in distilled water of the quality used in making the solution; but many drops produced no visible attack and in such cases the dissolved iron found in the liquid was small. A sharp distinction existed between drops causing breakdown and those causing none. Statistical experiments showed that the proportion of breakdowns observed in any given time increased as the concentration diminished, although at any given concentration it increased with time.

Other anodic inhibitors studied in the paper quoted were potassium ferricyanide and potassium chromate. Later, the inhibitive action of chromates was studied by Hoar,[80] who found that potassium chromate added to a ferrous solution at once produced a precipitate containing $Fe^{\cdot\cdot\cdot}$, $Cr^{\cdot\cdot\cdot}$, OH' and CrO_4''. He also abraded iron in air, and at once immersed it in potassium chromate solution; subsequently he isolated the invisible surface film by dissolving the metal in a solution of iodine in potassium iodide; the film was found to contain both iron and chromium. On specimens exposed to air for some time before introduction into chromate, the proportion of chromium found in the film was much smaller. These results suggest that the chromate converts *in situ* any ferrous hydroxide produced at weak points in the air-formed film to a mixture of ferric and chromic compounds, which seals the discontinuities and stops all attack. A prolonged air-exposure itself diminishes the discontinuities, so that the chromium taken up per unit area is smaller.

Effect of Treating Salt Solutions with Inhibitors. A quantity of an inhibitor which, added to pure water, would render it non-corrosive, may fail to do so if, say, sodium chloride is already present; the amount of inhibitor needed increases, in general, with the chloride concentration. When the immediate anodic product is ferrous chloride, which is merely converted to phosphate or carbonate at a distance from the point of attack, there can be no stifling. In order that corrosion shall be stifled by an anodic inhibitor, the latter must be kept in excess at the susceptible spots; the concentration in the body of the liquid must be such that it can diffuse up to those spots more quickly than ferrous ions can be produced by the electrochemical corrosion process.

Similarly for a cathodic inhibitor, whilst the direct deposition of (say) zinc hydroxide on the cathodic surface will diminish the rate of attack, this will not happen if sodium chloride is present at such a concentration that zinc hydroxide is only precipitated at a distance from the surface.

Adsorption Inhibitors. When a metal is immersed in any solution, the concentration of solute at the metal-liquid interface will, in general, be either greater or less than in the body of the solution; the distribution will always be such as to reduce the interfacial energy of the whole system to a minimum. It is believed that most salts are " positively adsorbed ", which means that their concentration is greater at the interface than elsewhere; very marked positive adsorption occurs in the case of many organic colloids. Where a strongly adsorbed substance is introduced into a corrosive solution, it will compete with other ions or molecules for accommodation at the surface, diminishing the amount of the corrosive substance present on unit area, and also the rate of replenishment. Friend [61] showed that many organic colloids such as agar, egg albumen and gum tragacanth greatly retard the action of acids or pure water upon zinc or iron; agar also represses the action of lead acetate or copper sulphate on zinc. Gelatine diminishes the action of sulphuric acid on iron, and Morris [113] has shown that, in doing so, it is removed from the body of the solution.

Adsorption may occur to a different extent on the oxide-covered and bare parts of a metal. Thus many adsorption inhibitors will act with special success either at the cathodic or the anodic region, so that there is no sharp distinction between adsorption inhibitors, on the one hand, and cathodic or anodic inhibitors on the other. Many pickling inhibitors (p. 144) are adsorption inhibitors acting specifically at anodic regions.

Cathodic Inhibitors

Calcium and Magnesium Salts. In addition to zinc salts, mentioned above, the salts of calcium and magnesium can in certain circumstances act as cathodic inhibitors—a matter of some importance owing to their presence in natural waters.

It will be convenient first to consider (Fig. 57) the behaviour of a nearly vertical iron plate partially immersed in magnesium sulphate solution.[38] Corrosion starts at susceptible points, and spreads downwards and sideways, just as in sodium sulphate (or chloride) solution, producing dome-shaped areas of anodic attack. Whilst oxygen exists in the liquid, the cathodic reaction takes place just above and outside these dome-shaped areas, but—in contrast to that obtained from sodium salts—the cathodic product, magnesium hydroxide, is sparingly soluble, and coats the iron around the dome. The layer formed seems to interfere with the cathodic reaction, by preventing oxygen in the liquid and electrons in the metal from coming close enough to each other to react. Anodic action then sets in at the coated area, and the ferrous salts formed interact *in situ* with the magnesium hydroxide, converting it first to a bright green hydrated magnetite and then to a pale brown ferric hydroxide, which, being formed from the original, adherent cathodic product, clings much more closely to the metal than ordinary secondary rust formed midway between anode and cathode. The brightness of the green and paleness of the brown (as compared with ordinary hydrated magnetite and ferric hydroxide) are probably due to the presence of magnesium; the green layer may perhaps contain a hydrated spinel such as $MgO.Fe_2O_3.xH_2O$.

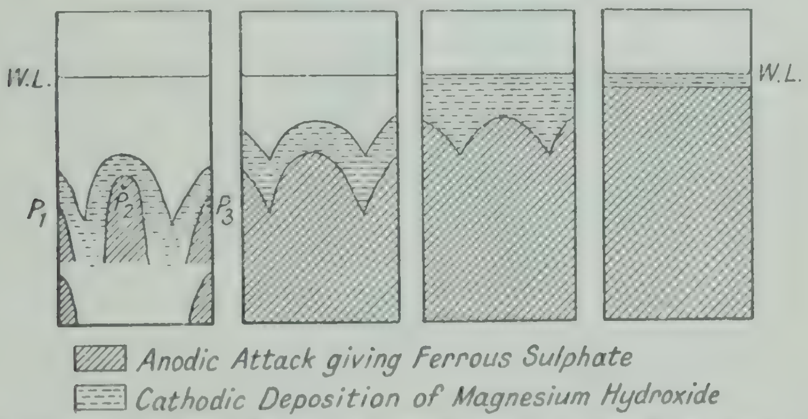

W.L.
P1
P2
P3
W.L.
▨ Anodic Attack giving Ferrous Sulphate
▤ Cathodic Deposition of Magnesium Hydroxide

FIG. 57.—Stages in Attack of Iron by Magnesium Sulphate Solution (Schematic).

Whilst the original cathodic areas are becoming anodic, the cathodic reaction is being pushed steadily upwards ; fresh areas become coated with cathodic product and then become anodic. Finally the cathodic reaction is confined to a strip about 1 to 2 mm. broad along the meniscus this strip becomes coated with a white layer, but, unlike the rest, it does not become green or brown. As the cathodic area is in the final stage narrow, and coated with a clinging substance which probably obstruct the cathodic reaction, the attack is much slower than in a sodium sal solution. In the author's experiments,[38] magnesium sulphate of all concentrations between 0·01M and 0·50M gave practically the same amoun of corrosion after twenty-six days ; very dilute solutions (0·001M) produced more rapid attack.

Calcium salts behave in a similar manner. In a solution of calcium bicarbonate, the main constituent of many natural waters drawn from chalk or limestone, the first cathodic product is doubtless calcium hydroxide ; but interaction with calcium bicarbonate quickly produces a layer of calcium carbonate, which is later replaced by hydrated magnetite and then by pale clinging rust possessing considerable protective properties

Hard Water flowing through a Steel Pipe. If a *hard* natura water containing calcium bicarbonate and oxygen is forced through a pipe-line, the incipient corrosion process should coat the interior with a protective coat of rusty chalk or chalky rust ; after the period needed for formation of this coating, the water delivered at the far end should be sufficiently free from dissolved or suspended iron compounds to be used for domestic purposes, including the washing of fabrics. This will not be true of the soft waters from igneous rock districts or the acid waters from moorlands, unless they have first been treated ; it will not even be true of hard waters, if they contain sufficient excess of carbonic acid to prevent the immediate precipitation of a calcium carbonate layer in physica contact with the steel. The latter type of water, however, may become less corrosive if it is cascaded through air, or if air is bubbled through it— processes which remove much of the excess carbonic acid, and also introduce oxygen. In film-forming water, oxygen usually exerts a favourable influence, ensuring that ferric rust is precipitated close to the metal ; i oxygen is deficient, protection by films is often less effective, and the water drawn from the far end of the pipe may contain enough dissolved ferrous compound to stain fabrics or ceramics by precipitating ferric hydroxide on subsequent exposure to air.

The Four Types of Carbon Dioxide. A solution containing calcium bicarbonate ($Ca(HCO_3)_2$) and nothing else can only exist at very low concentrations. Much higher concentrations of calcium bicarbonate can however, be obtained by shaking powdered calcium carbonate with water containing carbonic acid ; the higher the concentration of carbonic acid the larger the amount of calcium bicarbonate which can enter the water before equilibrium is set up with the solid calcium carbonate. Any water saturated with calcium carbonate and oxygen (e.g. one which has been shaken with marble dust and air) should, if brought into contact with iron, quickly deposit a chalky film which, although incapable of stopping corrosion entirely, can at least render it slow. If, on the other hand, the water contains more carbon dioxide than is needed for equilibrium, immediate precipitation of chalk cannot be expected, and a time-interval must elapse before the retardation of corrosion can be brought about. Any carbonic acid in excess of the amount needed to keep the calcium carbonate in solution is known as *Aggressive Carbonic Acid.*

It is possible to divide the carbon dioxide in a water into four parts :—

I. The carbon dioxide needed to form $CaCO_3$.
II. The carbon dioxide needed to convert $CaCO_3$ to $(Ca(HCO_3)_2$.
III. The carbon dioxide needed to keep the $Ca(HCO_3)_2$ in solution (i.e. prevent it from being metastable in relation to solid $CaCO_3$).
IV. Any other carbon dioxide present. This will be the Aggressive Carbon Dioxide or Aggressive Carbonic Acid.

Clearly the amounts of I and II in a given water are equal ; that of III depends on I or II, the relation being shown in Table XVI. The Free Carbonic Acid, as determined by the Water Analyst, represents only III and IV—provided that the titration is carried out rapidly ; the figure obtained on slow titration may include part of II.

TABLE XVI

RELATION BETWEEN THE DIFFERENT KINDS OF CARBON DIOXIDE
(J. Tillmans and O. Heublein)

Carbon Dioxide of the First Kind. mg/l.	Carbon Dioxide of the Third Kind. mg/l.
20	0·5
40	1·75
60	4·8
80	11·5
100	25·0
120	47·0
140	76·4
160	112·5
180	154·5
200	199·5

Notes (1) The carbon dioxide of the second kind is equal in amount to that of the first kind.
(2) Any carbon dioxide present in excess of the first, second and third kinds, represents aggressive carbonic acid (carbon dioxide of the fourth kind).

To test for the presence of Aggressive Carbonic Acid, the p_H of a water should first be determined. A sample is then left overnight in a stoppered vessel containing marble dust ; if next day the p_H value has risen, it is a sign that the original water contained Aggressive Carbonic Acid ; such a water is likely to give trouble on iron or steel. The criterion is of little value for zinc or lead, where protection depends more on the formation of a carbonate of the heavy metal than of calcium carbonate ; to test a water for plumbosolvency (power to dissolve the lead and thus become poisonous), it is better to leave a known quantity of the water in contact with a lead coil overnight, and estimate lead both in the liquid and in an sediment thrown down. It is commonly stated that any water containin *free* carbonic acid is capable of dissolving copper (see p. 48), but the fact are probably less simple.

Water-Treatment to avoid Aggressive Acid. Many acid waters fron igneous rocks or moorland districts attack iron pipes, producing damag to the pipes or discoloration of the water as delivered. Apart from th danger of perforation and leakage, the carrying power of the pipes may b reduced by the formation of voluminous tubercles—elongated blister full of magnetite. These troubles can often be reduced by passing th water slowly through beds of limestone, so as to ensure that the wate issuing from the beds is in equilibrium with calcium carbonate, or b treating the water with enough lime, sodium carbonate or sodiur hydroxide to neutralize the aggressive carbonic acid, or other acid presen (moorland waters often contain quinic and other organic acids derive from plants). Such treatment often greatly improves the behaviour o the water towards iron or steel, although sometimes it merely replace red-water complaints by tuberculation, which troubles the water consumer less but the water-undertaking more. The method is not we suited to water containing sodium chloride, for reasons explained on p. 12

It should be noted that the addition of the sodium hydroxide o carbonate merely serves to remove aggressive acid (carbonic or otherwise thus making the water a film-forming one. Unless a much larger quantit of alkali is added, it will *not* prevent the water from producing rust o *freshly abraded* iron. After sufficient soda has been added to remov aggressive carbonic acid, any further additions will be used up in pre cipitating calcium carbonate or magnesium hydroxide, and this "soften ing" action (however desirable from other standpoints) will not preven rusting and may even increase it. Only when precipitation of hardnes has ceased will further additions of alkali begin once more to raise th p_H value, and at that stage the total corrosion produced by the wate will decline. If chlorides and sulphates are not present in large amounts the water might, with sufficient additions of soda, become non-rusting t abraded iron, but such highly alkaline water would be unsuited for man purposes; if chlorides or sulphates are present, an ill-judged addition o alkali may convert comparatively harmless general attack into dangerou localized corrosion. In general, alkali-treatment is not carried so far a to give a completely non-rusting water.

Various complex sodium phosphates are being used in America fo the treatment of water before it is run through steel pipes or vessels The hexameta phosphate (*Calgon*) is the best known, and 2 to 5 part per million has often been found sufficient, although larger amounts ar required in the opening stages to build up a film. It can be used at low p_H (5·0–5·5) and has been recommended as less likely to caus tuberculation than lime treatment. Nevertheless, experience in Grea Britain seems to show that its behaviour varies with the condition (especially flow-rate). Calgon appears to be an adsorption inhibitor; th adsorbed compound may be a complex calcium phosphate, but this is uncertain, and it is not known whether deposition occurs at cathodic or anodic areas or both.

Sodium silicate is sometimes used to stop attack on steel pipes by aggressive waters, but its special function is the prevention of attack on lead pipes by soft or acid waters ; in this way, outbreaks of lead poisoning have been arrested. The silicic acid liberated by soft acid waters seems to be a specific inhibitor for lead, but sodium silicate does not always diminish the amount of lead taken up by hard waters reacting neutral or mildly alkaline.

Softening Treatment. Hard waters containing calcium and magnesium salts are often softened to reduce the wastage of soap in the household and at the laundry, or to prevent scaling and consequent overheating in boilers. In the soda-lime process, lime is added to convert calcium bicarbonate to calcium carbonate, and sodium carbonate to precipitate any calcium present as sulphate ; the precipitate of calcium carbonate is removed by filtration or sedimentation. If magnesium salts are present, sufficient excess of lime and sodium carbonate is introduced to yield sodium hydroxide, which, given sufficient time, should precipitate magnesium as magnesium hydroxide. This tends, however, to remain suspended in colloidal form, and usually arrangements are made to remove it in a *floc* of aluminium hydroxide by adding sodium aluminate. Sometimes crude aluminium sulphate and sodium aluminate are added ; these interact to yield a negatively charged aluminium hydroxide, which brings down the positively charged magnesium hydroxide. Sometimes the aluminium hydroxide is produced by simple hydrolysis of sodium aluminate. If the chemicals are added in suitable quantities, most of the calcium and magnesium salts can be removed, and the water, being in equilibrium with calcium carbonate, is free from aggressive acid, although capable of producing rust on freshly abraded iron.

Another method of softening is to run the water through a bed of *zeolite* (natural or artificial)—essentially a distended form of complex silicate containing sodium as one of the cations. The calcium ions in the water change places with the sodium ions of the zeolite ; when the zeolite mass becomes impoverished in sodium, it may be regenerated by passing sodium chloride solution through it. This method of softening does not reduce the total solids but merely replaces calcium bicarbonate and sulphate by sodium bicarbonate and sulphate ; both of these salts are corrosive at low concentrations. Moreover, since the amount of stabilizing carbon dioxide (type III in the classification of p. 131) needed for equilibrium falls off as the calcium content is reduced, a water which was non-aggressive before passage through zeolite may become highly aggressive after that passage, whereas soda-lime softening leaves water non-aggressive. It may be advisable to remove aggressive carbonic acid from zeolite-softened water by cascading, by treatment with a little lime, or by passage through limestone beds. The two last plans will again introduce hardness, but in small amounts ; actually a dead-soft water is not desirable for general supply purposes, and usually a certai proportion of raw water is by-passed at a softening plant, so as to leav a suitable amount of hardness in the " blended " water supplied to th consumers.

Sometimes, instead of zeolite, a resin is used for base-exchang purposes.

Anodic Inhibitors

Distribution of Attack. If a drop of sodium carbonate solutio of a concentration just insufficient to prevent attack completely is place on steel, corrosion will start along the drop boundary—the place whic with sodium chloride solution, would be immune. Similarly, a plat of steel partially immersed in sodium carbonate of border-line concentra tion will suffer attack along the water-line, which, in sodium chlorid would be free from attack in the early stages. If to a sodium chlorid solution increasing amounts of sodium carbonate are added, the lowe corroded area steadily contracts (Fig. 58, A, B and C), but, just as corrosio seems about to disappear altogether, a new zone of intense attack appear along the water-line (58 (D)); still higher concentrations of inhibito may prevent attack entirely (58 (E)). The corrosion produced at th water-line when both chloride and carbonate are present together occur at a much higher total salt concentration than in chloride-free carbonat solution (since more carbonate is needed to restrict the corrosion i presence of chlorides than in their absence), and both the total attac and intensity of attack is much higher. Thus a chloride-carbonat mixture of border-line composition is more destructive than a simpl carbonate solution of border-line composition.

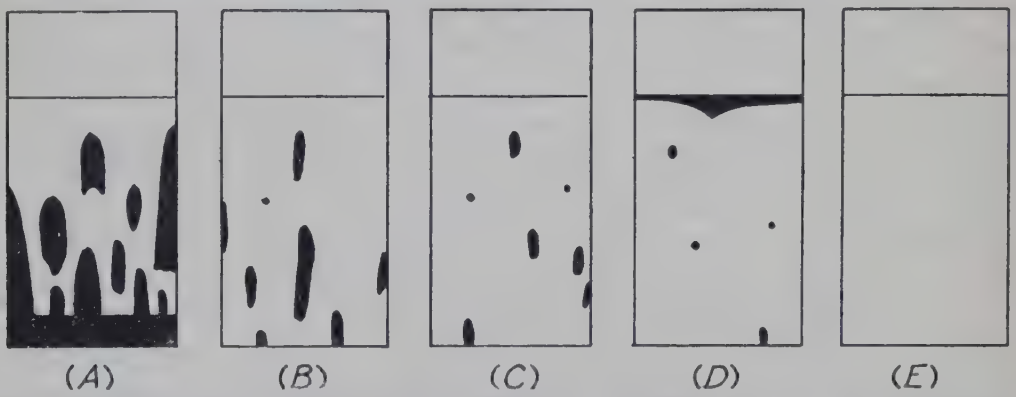


FIG. 58.—Corrosion of Steel by (A) Sodium Chloride and (B to E) Sodium Chloride with Increasing Amounts of Sodium Carbonate.

Dangerous Inhibitors. Sodium carbonate is called a dangerou inhibitor, because, if added in quantity just insufficient to abolish corrosio completely, it localizes the attack and renders it more intense than if n inhibitor had been introduced. Sodium hydroxide, sodium phosphate sodium silicate or potassium chromate are dangerous in the same sense The author [38] found, for instance, that the critical addition of one of thes inhibitors to a water containing sodium sulphate and/or chloride quickl perforated a steel sheet, generally at the water-line; the same water, without inhibitor, produced a larger total of attack in the same time, but no perforation, the corrosion being better distributed.

The intensification of attack is due to use of anodic inhibitor for dealing with a case where the control is cathodic.[42] The addition of the inhibitor *restricts the area* suffering corrosion, even when the amount added is insufficient to cause these areas to vanish completely. The cathodic area is not diminished, but, if anything, enlarged; thus the total corrosion will not, at first, be greatly altered, and the *intensity* of attack (corrosion per unit area of the part affected) will be *enhanced.* At first sight it might perhaps appear that the intensification would become infinite just before the anodic area has shrunk to zero; but this alarming expectation is not realized, since, when the anodic area becomes sufficiently small, anodic control and bottle-neck resistance begin to restrict the current flowing. Nevertheless, the intensification caused by insufficient treatment with an anodic inhibitor under conditions of cathodic control may very seriously increase the local rate of penetration as compared with an uninhibited system.

The particular factors leading to this dangerous state of affairs are absent when the inhibitor is cathodic or when the control is anodic. Nevertheless, a cathodic inhibitor may sometimes produce intensification of attack for other reasons. Thornhill [142] found that concentrated zinc sulphate solution gave a protective film which, however, broke down along the water-line, where attack was more intense than in an uninhibited system. There is some reason to think that a zinc hydroxide film may, in concentrated salt solution, pass to zinc oxide and acquire sufficient electronic conductivity to act as cathode, thus setting up the dangerous combination of big cathode and small anode.

Cause of Water-line Attack. It is not surprising that the special immunity met with at the water-line on steel partly immersed in sodium chloride, or at the drop margin under conditions of drop corrosion, should disappear when an inhibitor is added. The immunity can be attributed to the fact that the product formed at the cathodic zone along the water-line or drop margin is itself an inhibitor (sodium hydroxide). When the body of the solution contains an inhibitor, the probability of attack should become much the same everywhere. But it may still fairly be asked why the water-line zone (or drop boundary) becomes *more* prone to attack than the rest.

Actually it is found that many dissolution reactions in which metals are not concerned, proceed most readily at a water-line; a stick of sodium hydroxide half immersed in water is more attacked at the water-line than elsewhere. There may be more than one reason, but if, as seems likely, the orientation of molecules at a solid-liquid interface constitutes a barrier impeding the passage of molecules or ions across that interface, the disturbance of the orientation at the place where three phases meet should make passage easier than elsewhere. In the case of metals, however, two special reasons for the failure of inhibitor at such places can be suggested.

(1) Although sparingly soluble matter formed at the outset of th corrosion process at a susceptible spot, Q (Fig. 59), situated well awa from the water-line or drop margin, may adhere to the metal-liqui interface and stifle further action, the same substance formed at a simila susceptible point, P, situated in the meniscus of a partially immerse specimen, or at the margin of a drop, may adhere to the liquid-gas interface, so that stifling does not occur.

(2) Inhibitor is used up in stifling corrosion, and inhibition can onl be maintained if it is replenished at a suitable rate ; the tip of the meniscus at a water-line, or the angle formed at a boundary of a flat drop, constitut inaccessible " crevices ", where replenishment will occur more slowly tha anywhere else, so that the inception of attack is most probable at thes points.

Intense Attack at Contacts with Non-Conducting Substances

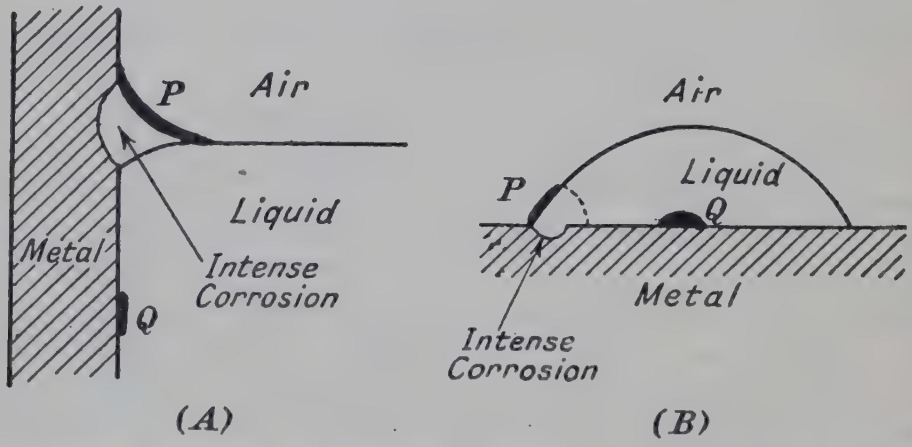


FIG. 59.—Intense Corrosion at Critical Concentration of Inhibitors (A) at Water-Line of Partly Immersed Specimen, (B) at Margin of Drop. At the Susceptibl Points, Q, the Product is precipitated in Physical Contact with the Metal and stifles attack, but at P it clings to the Water/Air Interface and attack proceeds unchecked.

Since crevices are also formed when the surface of a metal is screened by contact with some foreign body (e.g. a glass rod, or a string tied round the metal specimen), intense attack is sometimes met with at the screened area ; this will occur when the content of inhibitor is high enough to stifle attack over the main part of the surface, but not to prevent it in the crevice, either owing to lack of replenishment or by the corrosion product adhering to the wrong interface. Here again the dangerous combination of large cathode and small anode becomes operative. The danger is greatest if the liquid is in motion outside the crevice, although stagnant within it ; this will ensure replenishment of inhibitor at all points outside, so that attack will be confined to the crevice ; also the cathodic areas will receive a steady supply of the cathodic stimulator (usually oxygen, unless the anodic inhibitor itself acts as cathodic stimulator), so that the total current will be strong and the attack intense.

Pitting. Apart from intensification at water-line and places shielded by foreign bodies (e.g. glass or string), exceptionally susceptible places (e.g. sites of sulphide inclusions in iron) may in a chloride-carbonate or chloride-chromate mixture of border-line composition suffer anodic attack, with the rest of the surface acting as large cathode. If the secondary corrosion product accumulates on the metal (as on the upper side of a horizontal specimen), the anodic area may gradually spread, because the product screens an ever-increasing area of metal from inhibitor; if so, the attack should not remain intense. On the lower side of a horizontal plate or disc supported some way above the bottom of the containing vessel, the spreading of the anodic area may not occur, since the corrosion product falls away. Under such conditions small deep corroded areas (pits) may be produced, as found by Homer [85] using carbonate-chloride solutions of border-line composition.

Pitting or intensified corrosion is only likely to occur if the substance formed by interaction of the anodic product and the inhibitor assumes a membranous form, and produces over each pit a blister which prevents access of inhibitor to the actual site of attack. The sparingly soluble compounds of trivalent metals readily assume membranous form. Iron specimens rotated in chloride-chromate solutions of border-line composition suffer local attack which penetrates more deeply into the metal than that produced by a similar chloride solution free from chromate—although the total attack is less when chromate is present. Lead chromate does not easily assume a membranous form, and lead rotated in a chloride solution with a chromate concentration insufficient to prevent attack completely nevertheless suffers no intense corrosion, the action being well spread out—as shown in the work of Roetheli and Cox.[126] Recent work by Palmer at Cambridge suggests that, when a mixture of a phosphate and a strong oxidizing agent is used to inhibit the corrosion of iron, the blocking substance is ferric phosphate which does not readily form a membrane. Under suitable conditions, these inhibitive mixtures appear to be very efficient, even at temperatures up to the boiling-point and in presence of chlorides, and there is very little tendency to pitting even when attack is not completely arrested. The work is, however, in its early stages.

Oil Inhibitors. The "soluble oils" used for inhibitive purposes are clear liquids containing oil, water, soap and an amphipathic substance such as a fatty acid or alcohol. Hoar and Schulman [84] regard them as water-in-oil emulsions with particles too small to produce milkiness. When a small quantity is poured into a larger volume of water, an oil-in-water emulsion is formed which may be milky or clear, according to the size of the oil particles (increase in soap/oil ratio diminishes the size); each particle carries a negative charge. These emulsions may be quite stable, if large amounts of salts are absent. The addition of the oil greatly reduces the corrosive power of the water. The emulsified oil may act partly as an adsorption inhibitor, and give a thin oil film over the whole surface. Probably it is also an anodic inhibitor, since $Fe^{\cdot\cdot}$ ions, each carrying two positive charges, can neutralize and coagulate the negatively charged oil particles, so that blobs of oil are preferentiall formed over just those points where corrosion would otherwise start, an consequently prevent it from starting. But, just because these oils ar anodic inhibitors, they will permit intensified attack at places wher screening prevents replenishment, e.g. where string is tied round a ste specimen, as in the experiments of Hamer, Powell and Colbeck,[72] whos paper presents a good account of the uses and limitations of oil inhibitor The oils must be regarded as belonging to the dangerous class, and ma if added in insufficient quantities, make matters worse.

Inhibitive Water Treatment in Industry

General. Watery liquids used in industry are often treated wit inhibitors to prevent corrosion of the metal with which they will com into contact, but other chemicals are generally added at the same tim for different—and possibly more important—purposes. Thus refrigeratin liquids usually contain high concentrations of salt to depress the freezing point, cooling-waters at chemical works may be treated with algicides t prevent growths in the cooling jackets, whilst in boiler waters the firs concern is to prevent a badly conducting scale forming on walls throug which heat must pass.

Freezing Brines. The liquids used in commercial refrigeratio consist of concentrated solutions of sodium and/or calcium chloride sometimes magnesium chloride is used—often along with calcium chlorid The sodium brines are the most troublesome, causing attack on iro and, if the tanks or pipes are galvanized, on the zinc also; the sodiu hydroxide formed at the cathodic area near a water-line may cree upwards, and soften or loosen any paint which it reaches. Calcium an magnesium brines are relatively free from this tendency, and owing t the sparing solubility of the cathodic product cause less corrosion, les discoloration of the brine and less interference with heat transfer due t rust on the walls. Nevertheless, even calcium chloride brines may wit advantage be treated with sodium chromate (generally added as a mixtur of sodium dichromate with sodium hydroxide or sodium silicate), and thi considerably cuts down attack without entirely preventing it. It ma excite surprise that chromates can be beneficial at this high chlorid concentration, but actually just because of the large amount of chlorin ions, the corrosion product (a very adherent dark-coloured scale) is produced over the whole surface, and, since there are no uncoated areas t act as efficient cathodes, there is less pitting than in brines free from chromate. Even the total corrosion is less—for a given chromate concentration—in a concentrated chloride solution than a dilute one; this ma be partly due to the lower oxygen-solubility.

Chromates are skin-irritants, and for some purposes it is better to trea brines with sodium phosphate or with zinc dust; the latter doubtless takes up oxygen and temporarily stops corrosion, whilst the formatio of zinc chloride—a cathodic inhibitor—may give more lasting relief.

Cooling-Waters. In numerous chemical processes, liquids are cooled by passage through tubes surrounded with cold running water or through vessels within which are suspended coils of tubes along which the cooling-water is forced. If the water is corrosive, the deposition of rust may reduce the heat-transfer, or block the water-flow, whilst, if the attack is localized, perforation may occur. Somewhat similar problems arise at metallurgical works, where furnaces are often water-jacketed. The waters used may not be specially corrosive as drawn from the source, but they often pick up acidic substances when they are passed down cooling towers to get rid of the heat which they have picked up in performing their function; sometimes sulphur dioxide (or hydrogen chloride) are present, and everywhere there is carbon dioxide. A factor adding to the expense of inhibitive treatment is the loss of water from the cooling towers as spray or vapour; spray losses are particularly serious, as the droplets escaping carry away valuable inhibitor, and the towers should be designed to minimize spray loss. Vapour loss necessitates the introduction of raw water as " make-up ", and, if the raw water should itself be corrosive, this involves fresh consumption of inhibitive chemicals.

The inhibitive treatment varies greatly with conditions. If the volume of the cooling system is small and the plant valuable, it may be good policy to add sufficient chromate to make the water completely non-rusting. Chromates are used at transformer stations, in the oil industry, and sometimes in the cooling-water of air-conditioning plants. The chief objection is that if insufficient is added the attack may be localized and intensified. It is difficult to give any universally applicable estimate of the concentration required, since the risk of a spot becoming impoverished in chromate depends on the geometry of the plant and the rate of flow, as well as on the temperature and chloride concentration of the water. One authority mentions 0·05% potassium dichromate for protecting iron at 20° C. and 0·2% at 80–90° C., further increases being recommended if the iron is in contact with brass; concentrations exceeding 1% may be necessary in waters containing chlorides. In discussing the use of sodium dichromate for steel cooling jackets in power rectifiers, van Brunt and Remscheid[146] emphasize the need of keeping the concentration sufficiently high if chlorides are present; they consider an addition of 1½% normally sufficient in water otherwise suitable for cooling. Great care must be taken that no points are screened from chromate-supply, otherwise cells with large cathodes and small anodes will lead to intense attack. The avoidance of re-entrant corners, crevices and cracks is a matter for the plant-designer, but the removal of any deposit capable of acting as a chromate-screen is the affair of the plant-user. Loose scale and tubercles of old rust are described as the " arch-promoters of corrosion ".

Other anodic inhibitors—like sodium carbonate or silicate—are even more dangerous, and cases are known where intense pitting has followed their use, notwithstanding a reduction of the total corrosion. Nitrites, although also belonging to the dangerous class, are increasing in popularity as inhibitors, and are employed at chemical works and in the oil industry Their behaviour is, however, somewhat variable.

Where the volume of cooling-water is very large, the use of chromate may not be economical, and water treatment may be confined to the addition of sufficient alkali to neutralize any acid present in the raw water or taken up in the cooling towers. Lime and sodium carbonate have been used in such cases, and, whilst the water is not rendered non-rusting towards freshly abraded steel, the performance of the cooling system can be greatly improved ; provided that the alkali addition is not carried so far as to remove the whole hardness due to calcium bicarbonate, the rate of attack is not likely to be increased, even locally, by such additions Emulsifying oils have been seriously considered for addition to cooling waters, but, where chlorine or hypochlorites have also to be added to prevent algæ, they interact with the oil, so that each addition reduces the efficiency of the other.

At one American metallurgical works, where the water picked up acid fumes before entering cooling jackets, the addition of white arsenic was found to be a remedy ; this cannot be recommended for general use.

Boiler Feed Waters. The main object of treating boiler water is to prevent the formation of a hard, badly conducting scale on walls or tubes through which heat has to pass. If such a scale is produced (in addition to the drop in thermal efficiency and increase in fuel costs), overheating will lead to oxidation on the fire side, causing serious distortion and blistering of the steel, with a risk of burst tubes. The nature of the solid first deposited on evaporation determines whether an adherent scale appears, or a harmless loose sludge which can be got rid of by a blowdown. Calcium carbonate or phosphate usually form a sludge, but calcium sulphate and certain silicates produce a scale ; when once a scale has started to grow, carbonate is often found in it. Silicate scales are particularly bad conductors of heat, and, being hard and difficult to remove, should be avoided at all costs. Oil, if deposited on (or in pores within) scale, increases the obstruction to heat, and consequently oil must be kept out of boiler feed water ; if present in emulsified form, it may be entrapped in a floc of aluminium hydroxide, produced in the manner described on p. 133.

Clearly the smaller the amount of dissolved solids in the water entering the boiler, the less will be the deposition on the walls. Large power plants make use of condensate from the engines to feed the boilers, the same water passing round the system over and over again. This minimizes introduction of solids, but a small amount of make-up is always needed to replenish losses, and sometimes this is softened by one of the methods described on p. 133, or—better still—distilled before being pumped into the boiler. If not distilled, the water should be “ conditioned ” by addition of sodium phosphate or carbonate in quantity sufficient to ensure that, although evaporation must increase the concentration of *all* substances present, the solubility product of a *sludge-forming* salt is reached *before* that of a *scale-forming* salt; sometimes colloidal substances are added, which militate against the production of hard scale.

Among the conditioning chemicals, sodium carbonate suffices for use in low-pressure boilers, but at temperatures prevailing in the modern high-pressure boiler, it would be decomposed, giving sodium hydroxide, which would be an unsuitable conditioning substance, besides introducing the risk of caustic cracking (p. 110). In such cases, sodium phosphate should be used; this is sometimes introduced as hexametaphosphate (*Calgon*) which is converted to ordinary phosphate at boiler temperatures —a plan that reduces the risk of the deposition of solid calcium phosphate in the feed-lines, pumps and valves.

Having brought the water to a condition calculated to deposit sludge rather than scale on evaporation, it is next necessary to render it non-corrosive. This involves addition of sufficient alkali to keep the p_H between about 10·4 and 11·0—a range where the hydrogen-evolution type of attack is slow, and where the solubility of the immediate corrosion product, ferrous hydroxide, is low, so that corrosion tends to stifle itself. In addition the oxygen concentration must be kept down (for boilers working above 400 lb./sq. in., the oxygen should not exceed 0·02 c.c./l., although in low-pressure boilers, 0·05 c.c./l. may be permitted). The ferrous hydroxide film produced on the steel probably interacts with water to give magnetite (p. 38) but provided that the magnetite layer is continuous, it should be protective. When oxygen is present, it will convert ferrous hydroxide to magnetite or ferric hydroxide at a distance from the surface; since such conversion must render the water unsaturated with ferrous hydroxide, a continuous film may not be formed. Unpublished work carried out by Gould at Cambridge suggests that this is the reason why boiling water in presence of oxygen produces localized corrosion.

In boiler tubes carrying mill-scale, the scale will act as an efficient cathode if oxygen is present, causing intense corrosion at discontinuities where the exposed steel constitutes a small anode. Turner [145] has shown that, in locomotive boiler tubes, pitting does occur where the oxide scale has been cracked by the bending or straightening of tubes, or even by rough handling. He advises the removal of oxide scale by shot-blasting. This is sound advice, but pitting can occur on descaled steel if oxygen is present.

In plant where condensate is largely used for boiler feed purposes, much trouble may be avoided if precautions are taken to prevent air reaching the condensate, which when first formed is free of oxygen. The make-up water will, however, still require de-aeration. The removal of the greater part of the oxygen is in most plants carried out thermally by spraying the water into a partially evacuated chamber, heated by exhaust steam or otherwise, or by running it down trays in a similar environment. This may reduce the oxygen content to 0·05 c.c./l., or perhaps lower, but it is impossible to remove the last traces of oxygen by thermal methods alone; at large power stations, it has become customary, after thermal de-aeration, to add sodium sulphite, which combines with the residual oxygen. Sufficient time must be allowed for the sulphite to act before the water enters the economizer. The rate of combination between sulphite and oxygen depends largely on temperature and the excess of sulphite used. Certain substances present in moorland waters retard the change, but copper salts (usually present if the feed pumps are of bronze) accelerate it.

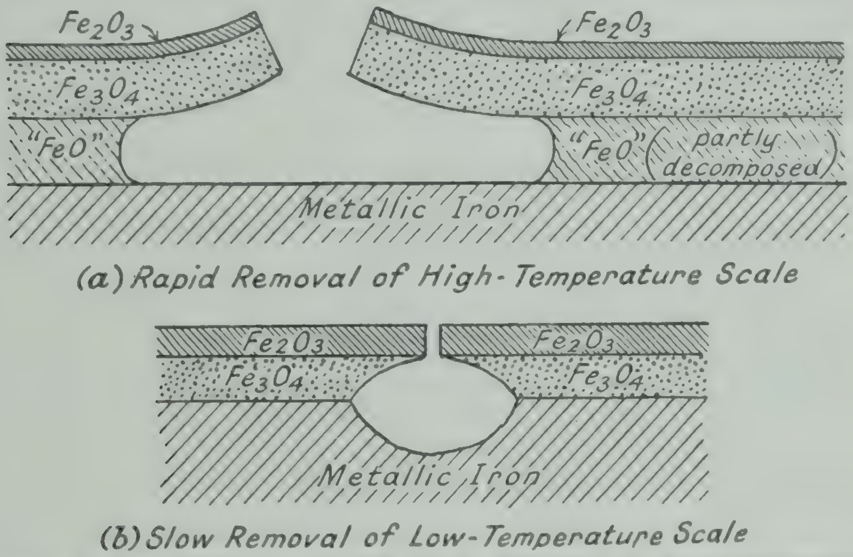
The use of bronze feed pumps is a subject much discussed to-day. In some plants attack has occurred on bronze impellers; this may have been due to traces of ammonia or carbonic acid in the waters passing through them. The copper is usually redeposited either as metal or as oxide on the steel within the boiler; whether this produces corrosion will depend on the chemical state and distribution of the copper, but certain cases of serious corrosion have been reported which may be due to redeposition of copper. There is to-day a tendency to adopt stainless steel pumps.

Pickling Processes to Remove Scale and Rust

General. The removal of mill-scale and rust from steel is absolutely necessary before a protective coat of non-ferrous metal can be applied (by any of the processes described in the next chapter); a similar removal is generally advisable before painting, if the best protection is to be obtained. Wire-brushing removes loose scale and rust, but leaves adherent scale and some residual rust; the burnishing action of the wire-brush may confer on the scale a metallic lustre which has deceived experienced observers into thinking that the scale has been removed. Sand-blasting really does remove scale and rust, but is dangerous to health, owing to the risk of silicosis. Shot-blasting is safer, and, if the type of shot is carefully chosen, the surface is left in a peened condition—more resistant to corrosion fatigue than at the outset (p. 122). Abrasive wheels, chipping hammers and other impact descaling tools are used for special purposes. All these methods require, however, special equipment; where this is not available—and especially for small articles—pickling in acid is generally employed to remove scale and rust. Pickling is also used to remove the chalky deposits thrown down where hard waters have passed through pipes, and in all cases it is necessary to take precautions to minimize attack on the metal during the operation.

Different Types of Mill-Scale. The simplest method of pickling steel is to immerse it in warm dilute sulphuric or cold hydrochloric acid, with some brushing or scraping if the scale proves stubborn. It is still widely believed that descaling by pickling depends essentially on the dissolution of the iron oxides in acid giving the corresponding iron salts. Two facts suggest that this belief is wrong: first, a residue of undissolved scale fragments is usually found at the bottom of the pickling tank: secondly, the iron salts found in the bath are almost entirely ferrous. Actually, the direct attack by acid upon ferric oxide and magnetite is extremely slow. A "reductive attack", due to the cells

Fe | Acid | Fe_3O_4 or Fe | Acid | Fe_2O_3, can, however, occur (p. 42). A distinction should be drawn between the scale formed when the rolling has finished above and below 575° C. respectively. Steel emerging from the rolls above 575° C. will carry three layers, the bottom one having a composition approximating to FeO, although on further cooling the ferrous oxide will partly decompose into a fine mixture of Fe and Fe_3O_4; this provides large numbers of microscopic cells Fe | Acid | Fe_3O_4, so that it is easy for the acid to eat its way along the decomposed layer, allowing the outer part of the scale to peel off (Fig. 60 (*a*)). Thus steel finished above 575° C. is readily descaled by pickling. On steel finished below 575° C., the FeO layer is usually absent, and consequently the finely divided Fe + Fe_3O_4 is not formed (Fig. 60 (*b*)). However, the cell required for undermining does exist wherever a crack penetrates to the base of the scale, and the destruction of the magnetite and the iron on which it rests makes it possible to undermine the rest of the scale; for geometrical reasons, this is a slower process than the descaling of steel finished above 575° C., and descaling of cold-finished steel is apt to be a sluggish and unsatisfactory operation.



(a) Rapid Removal of High-Temperature Scale

(b) Slow Removal of Low-Temperature Scale

FIG. 60.—Modes of Removal of Scale by Pickling in Acid (Diagrammatic).

Attack on the Steel during Pickling. Whilst the last obstinate patches of scale are being removed, the acid continues to attack the metal at the regions already bare. This has six undesirable results:

(*a*) The consumption of acid becomes excessive.
(*b*) There is destruction of valuable metal.
(*c*) The pickling room becomes filled with acid spray, due to the bursting of hydrogen bubbles, which is unpleasant and even detrimental to health.
(*d*) The surface becomes roughened, which adds to the cost of grinding and polishing if the metal is to be electroplated (if galvanizing or enamelling is intended, a certain degree of roughness may be an advantage).

(*e*) The cathodic reaction in acid pickling is the discharge of hydrogen ions; owing to the sluggishness of the reaction $H + H = H_2$ the hydrogen is not entirely evolved as gas bubbles at the surface but may enter the metallic lattice as H atoms (which can occupy interstitial positions in the lattice and readily diffuse inwards or perhaps as protons and electrons. Some of this may b evolved as molecular gaseous hydrogen at cavities within th metal, usually associated with inclusions, producing high interna pressures.[33] If the rolled metal contains inclusions just below the surface, the hydrogen liberated internally may force up th surface layer as *blisters* (see p. 111).

(*f*) If an attempt is made to bend freshly pickled iron, the hydrogen in the lattice opposes gliding, and thus prevents plastic flow whilst not to the same extent preventing fracture. On th contrary, deformation aids the internal liberation of hydrogen and the pressure produced at any internal cavity may cause it to extend into a crack. The further the crack spreads, the more high-pressure hydrogen is liberated in it, so that the propagation of a hydrogen crack is like the spread of an explosion. This *embrittlement* of freshly pickled steel is one of the main objections to pickling. It occurs particularly with steel carrying sulphide inclusions, because hydrogen sulphide is a positive catalyst for the anodic reaction, thus increasing the cathodically liberated hydrogen, and a negative catalyst for the reaction $H + H = H_2$, thus building up a high surface concentration of atomic hydrogen. High-carbon steels which have been hardened, tempered and deformed, may actually crack during pickling. This does not occur with mild steel, and the embrittlement largely disappears on storage for some days at room temperature or on half an hour's immersion in hot water, which is more effective than air at the same temperature; the recovery of ductility is due to the escape of the hydrogen, but, if the change has been sufficient to injure the structure (e.g. by starting incipient cracks), such damage cannot be repaired merely by storage.

Inhibitors. In order to avoid the six objectionable occurrences mentioned above, it is usual to add to the acid an inhibitor designed to retard attack on the metal without interfering with the removal of scale. Many common colloidal substances, such as gelatine, agar or tannin, possess some inhibitive action, whilst tin salts repress the special attack on sulphur-rich steels containing little copper (p. 49). Among pure chemicals quinoline ethiodide received considerable study in early laboratory work on inhibition, but to-day more complicated bodies are used in industry, containing sulphur as well as nitrogen; one commercial inhibitor contains di-ortho-tolyl thiourea; another is based on dihydro-thio-ortho-toluidine.

The efficiency of inhibitors generally falls off as the pickling temperature rises. Moreover an inhibitor may overcome some of the six troubles enumerated above without curing the others. For instance, glue is effective in cutting down consumption of acid and evolution of hydrogen spray, but hardly affects embrittlement, which depends, not on the hydrogen evolved as gas, but on hydrogen entering the metal. As shown by Morris,[113] control of diffusing hydrogen does not necessarily go with control of evolved hydrogen. Indeed, a substance which prevents the emergence of hydrogen may actually increase the amount available for internal evolution.

Different explanations have been proposed for the action of pickling inhibitors, and possibly the mechanism is not always the same. Some have asserted that the hydrogen overvoltage is raised, thus repressing the cathodic reaction; quinoline ethiodide is said to act in this way. Others hold that the colloidal inhibitors are preferentially deposited on anodic spots, the colloid particles being discharged by the iron ions formed there at the outset of the process, so that the anodic reaction is stifled. Unpublished research by Hoar shows that all types of pickling inhibitors raise the corrosion potential of steel—indicating that anodic inhibition prevails—although sometimes cathodic inhibition occurs also.* Probably the inhibitors in commercial use, which contain both nitrogen and sulphur atoms, anchor themselves to the metal by these atoms, in such a way as to screen the surface, inhibition being most effective if a single molecule can screen a relatively large area of metal. It is considered that the layer formed by the attached molecules is discontinuous, but may nevertheless interfere with the replenishment of acid to the required points on the surface, as well as the removal of iron salts from the points of attack. More research will be needed before the matter is fully understood.

Phosphoric Acid Pickling. Articles pickled in hydrochloric and sulphuric acid are apt to rust when subsequently exposed to air. Fears have been expressed that paint applied over rusty surfaces gives poor protection, and sometimes the surfaces are dipped in lime or soda to remove acid traces before painting (soda may introduce a new danger, as a trace of alkali left on the metal may soften or loosen the paint). A better plan is to finish the pickling in phosphoric acid. In *Footner's duplex process*,[60] much used in pickling plates intended for building oil storage tanks and the like, the scale is removed by 15–20 minutes' immersion in 5% sulphuric acid at 60° C., followed by two dips in water at 60°, and finally a 3–5 minutes' dip in phosphoric acid at 85° (this should contain 2% phosphoric acid and 0·3–0·5% of iron when fresh, the composition being approximately maintained by addition of phosphoric acid). The steel emerges carrying a dull grey film of iron phosphate, which gives temporary protection against atmospheric attack and forms a good basis for paint. The plates, which, being already hot, dry rapidly in air, should be painted before they cool.

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* This simple method of distinguishing anodic and cathodic inhibitors has been much used by Hoar; the graphical construction shown in Fig. 35 (p. 68) indicates that any substance which hinders anodic action and steepens the anodic polarization curve, must raise the potential given by the intersection point. Conversely, cathodic polarization must lower the potential.

Electrolytic Pickling. If the articles to be pickled receive anodi or cathodic treatment in the pickling bath, some of the troubles of plai pickling are avoided, although sometimes others may be enhanced. Thu anodic pickling avoids embrittlement or blistering due to hydrogen, bu may stimulate attack on the metal. Cathodic pickling reduces the attac on the metal, but may introduce additional hydrogen.

The *anodic* treatment is best carried out by *Laban's process.* Th steel articles are made anodes at about 100 amp/sq. ft. in 30% sulphuri acid, containing potassium dichromate; this leaves the steel passiv with a clean satin finish, probably produced by the mechanism simila to that responsible for anodic polishing (p. 104).

The *cathodic* treatment is usually carried out in sulphuric acid, an it is claimed that in pure acid no hydrogen is taken up. If arsenic o selenium is present, hydrogen enters the steel, which may becom extremely brittle, snapping when an attempt is made to bend it. I seems that arsenic, whilst not interfering seriously with the discharge o ions to give atomic hydrogen, prevents emergence from the metal a hydrogen gas. At any internal rifts or cavities there is no opposition t the production of gas (arsenic, etc., being there absent), and thus larg internal pressures can be developed, with consequent embrittlement o blistering.

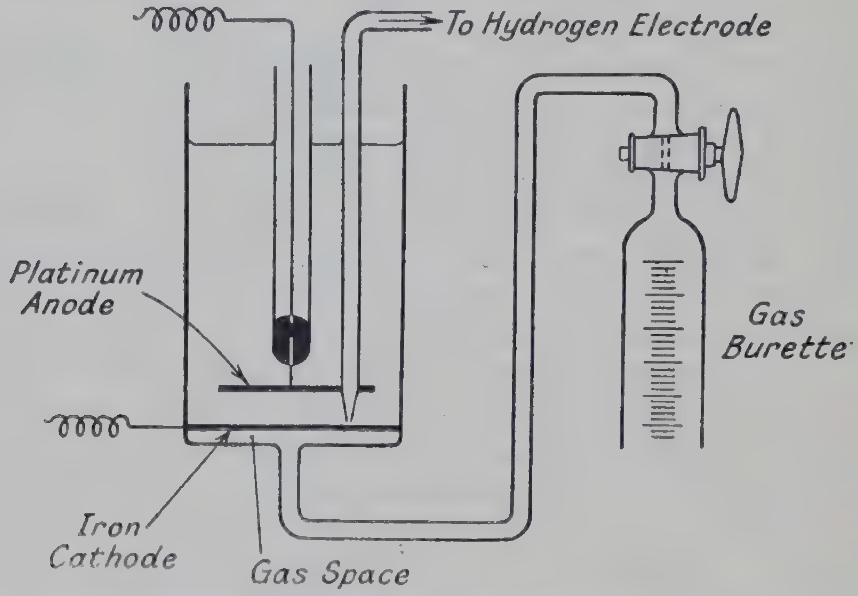

Fig. 61.—Collection of Hydrogen forced through an Iron Cathode (A. H. W. Aten and M. Zieren).

The correctness of this explanation is shown by the classical experiments of Aten,[3] who used an electrolytic cell with the cathode at the bottom and a gas space below it (Fig. 61). When the electrolyte is fre from arsenic, little hydrogen is evolved in the chamber below the cathode but when arsenious oxide (or a mercury salt) is added, gas begins to b collected in the burette. This would seem to be due to hindrance of ga evolution on the upper surface, since there is a marked depression in th potential which indicates the accumulation of a considerable concentration of electromotively active (atomic) hydrogen, thus providing the concentration gradient needed to maintain movement of hydrogen through the iron to the lower surface, where, arsenic being absent, evolution as gas is easy.

Cathodic treatment in (aqueous) alkaline solutions is used before plating to remove grease and other contamination, but does not serve to remove scale. However, if the electrolyte is fused alkali, the scale is reduced to a metallic sponge which readily leaves the surface. In the *Tainton process*—used for cleaning wire before the electrodeposition of zinc—fused sodium hydroxide at 450° C. is employed, the anode being iron or nickel; it is claimed that no hydrogen is absorbed.

Electrolytic Pickling with Inhibitors. In a process described by the Austrian electrochemist, Machu,[104] cathodic pickling is conducted in acid containing an inhibitor. The advantage is that the current density (1 amp./m.^{2}) is less than 1/100 that used in plain cathodic pickling, whilst the inhibitor concentration ($< 0{\cdot}01\%$) is less than 1/10 that used in currentless acid pickling. Moreover, the combined process avoids the main disadvantage of each simple method—namely the organic films left on the surface when inhibitors are used at high concentrations, and the fear of hydrogen brittleness often associated with cathodic pickling at high current density.

In the *Bullard-Dunn process*, developed in America and much used in the automobile industry, the article to be descaled is made the cathode in a hot acid sulphate bath containing a trace of tin salt. So soon as the steel is exposed at any point, a very thin layer of tin is deposited there, and the formation of hydrogen ceases, owing to the high overpotential of tin; thus the action is diverted elsewhere, and on objects of irregular shape, even the recesses are soon found to be losing their scale. The tin film (far thinner than ordinary plating) protects the metal sufficiently to prevent roughening, which would increase costs of subsequent grinding and polishing; moreover, since practically no hydrogen enters the steel, there is no embrittlement. Ferric salts must be excluded from the bath, since otherwise current would be wasted in reducing them to the ferrous condition; consequently a silicon iron anode is used, which (owing to the presence of a film, mainly silica, formed upon the surface) avoids the anodic oxidation of ferrous to ferric ions.

Inhibitive Pretreatment

General. In most cases, the beneficial action of a soluble inhibitor added to a water lasts only as long as a sufficient quantity of the inhibitor is maintained in that water. For instance, bright iron placed in a typical tap-water treated with potassium chromate remains free from rust, but if taken out and placed in the same water free from chromate, it soon develops rust. The after-effect of chromate treatment may, however, be prolonged by special methods of procedure. The author[44] placed specimens of iron, previously etched in acid, in water containing chromate and chloride in such proportions that the more susceptible parts of th iron accessible from the surface were dissolved away, leaving the res passive ; if, after rubbing away the loose corrosion product, the specimen were then taken out and placed in a natural water, it was found that th time needed for the appearance of rust was about 100 times as long a that taken for rust to appear on untreated iron placed in the same water— although the absolute times varied very much from one water to another

Numerous commercial chemical or electrochemical processes have bee developed to produce films—usually visible—on iron and other metals calculated to improve resistance to corrosion in environments containin no inhibitive constituent. These mostly depend upon treatment i chromate or phosphate solutions. Some are intended for surfaces whic cannot be painted, so that the protection is due to the film left by th inhibitive treatment, aided by any oil which may be applied and whic is held in the pores of the film. Other processes aim at producing a fil upon which a paint coat is later applied, the idea being to reinforce th protective action of the paint, and also to provide a surface into whic the paint coat will interlock, thus improving its mechanical adhesion much of the apparent improvement in the adhesion brought about by suc processes lies in the fact that, owing to the inhibition of corrosion, th production of bulky rust below the paint and of alkali (at the cathodi points) is avoided ; rust and alkali are the important causes of peelin or blistering in paints applied to surfaces which have received n pretreatment.

In general, thorough removal of scale and rust by pickling or otherwis is needed before the inhibitive chromate or phosphate bath is allowed t act on the metal to produce the film. Certain processes have been pu forward which aim at avoiding the need for pickling or other cleaning some have claimed to convert rust to compact phosphate or other harmless substance, and to render the iron passive at breaks in the mill-scale so that the E.M.F. of the cell iron | scale is reduced to zero. It cannot be stated that any of the commercial processes which aim at dispensin with thorough preliminary cleaning have proved, on being tested b impartial investigators, to be completely satisfactory, although it is no impossible that further research may lead to an inhibitive wash which wil avoid the necessity of removing rust and scale. The sections which follo are confined to a consideration of processes which have proved useful i producing protective layers on previously cleaned metal.

Iron and Steel. If iron is placed in a solution of phosphoric acid there is some attack at first, but when the layer next to the metal ha become saturated with iron phosphate, attack slows down, as a fil of solid iron phosphate develops. If the acid is already saturated wit iron phosphate, the building up of the film can start at once, and, sinc the expenditure of acid in attacking the iron will diminish the amoun of phosphate which can be held in solution, a further quantity of soli phosphate is deposited along with that formed by attack on the basi metal. Numerous processes involving phosphoric acid containing phosphates have been proposed; it will have been noticed that in Footner's pickling process [60] (p. 145) it is recommended that the phosphoric acid used should contain iron phosphate. But films consisting solely of iron phosphate possess the disadvantage that the oxidation of ferrous to ferric phosphate involves volume changes and loss of protective power. Thus in modern protective processes, the phosphoric bath contains phosphates of zinc and/or manganese, and these are thrown down when the acid attacks the iron. Details are complicated since most metals form at least three phosphates, the type $M(H_2PO_4)_2$ being more soluble than $MHPO_4$, whilst $M_3(PO_4)_2$ is least soluble of all (M is here assumed to be divalent). But the principle is simple; as the acid attacks the metal, the solution becomes increasingly supersaturated towards one or other solid, which is consequently deposited.

However, if the cathodic reaction in such cases is the evolution of hydrogen or the reduction of any oxygen which may reach the metal, film formation will be slow and irregular; by adding copper salts, or an oxidizing agent (such as an organic nitro-compound), provision is made for a smoothly running cathodic reaction, and the process becomes much faster. Times measurable in seconds are now possible.

Commercial processes based upon these principles include *Parkerizing*, which is intended for use where no paint is to be applied, whilst *Bonderizing* and *Granodizing* are intended as a basis for paints or stoving enamels.

Phosphate processes are largely used before the application of paints and enamels by manufacturers of automobiles, cycles, typewriters and metal furniture. The coating is usually dark grey, and the performance of the paint is certainly improved by such treatment, except when the environment is exceptionally acid; in the latter case, tests have suggested that steel covered directly with paint fares better than that carrying a phosphate coat below the paint, owing to the action of acid on the phosphate. But, in any case, steel coated with ordinary paint is unlikely to afford satisfactory protection against acid.

Zinc and Tin. Protective coatings of zinc or tin are often applied to iron, and sometimes the coats themselves receive an inhibitive treatment, which may serve to diminish the rate of attack on the covering, and also on the iron exposed at pin-holes; but it will also tend to diminish cathodic protection. *Granodizing* and *Bonderizing* are both employed for producing a phosphate layer on zinc or zinc-coated iron. Other methods depend on chromates; the plan of immersing a newly galvanized surface in chromate solution whilst still hot has long been practised in some American works. In the *Cronak process*, zinc-coated steel is carefully degreased, dipped in warm water and then in a solution of sodium dichromate and sulphuric acid for 10–30 seconds. A similar process is used for articles of solid zinc alloy, e.g. automobile door locks. Protective films can be formed on tin-coated iron (tin-plate) by immersion after degreasing in hot chromic acid, or in hot alkaline solution containing phosphates and chromates—a solution which performs its own degreasing.

Aluminium and its Alloys. In the *MBV process*, articles are dipped in a boiling liquid containing sodium carbonate (5%) and sodium chromate (1·5%) for 3–5 minutes; if sodium hydroxide is present, lower temperature (30–40°C.) can be used, but a longer time (30 minutes is needed. The film formed considerably increases the chemical resistanc of aluminium and its copper-free alloys, and a certain amount of foldin of sheet is possible without rupturing it; the mechanical hardness i increased by treatment in 3–5% sodium silicate at 90° C. for 15 minutes which also serves to seal pores in the film. In the *Alrok process*, article after immersion in a hot carbonate-dichromate are sealed in hot dichromate which improves the corrosion-resistance further.

Still better protection is obtained if the aluminium is subjected t anodic treatment, which builds up an oxide film of considerable thickness The process, known as *anodizing*, was first successfully worked out by Bengough and Stuart, who recommended, as electrolyte, 3% chromic acid at 40° C. with an E.M.F. of 40 volts, gradually raised to 50 volts Sutton and Sidery[133] prefer to raise it gradually from 0 to 40 volts in 15 minutes, maintain it at 40 volts for 35 minutes, then raise it to 50 volts in 5 minutes and keep it there a further 5 minutes. Steel cathodes are generally used. The fact that the film is a non-conductor ensures that irregularly shaped articles are coated all over; after the parts nearest to the cathodes have been covered, the process is diverted to the remote parts. Thus the "throwing power" (p. 153) of the process is good, and, by placing the cathode outside a long tube, it is possible to coat the whole interior.

Another bath used in anodizing contains sulphuric acid with glycerine, aluminium sulphate or glycol. The hardness and other properties of the skin are varied by altering the acid concentration (10–70%), E.M.F. (10 volts upwards) and time of treating (10–50 minutes). Soft malleable films are needed on material intended for bending or fabrication, and hard films on finished articles. On the whole, the higher the voltage, the harder the film. Lead cathodes are commonly employed. Yet another bath is based on oxalic acid, and is used with A.C. superimposed on D.C. The films obtained by anodizing are sometimes rendered more resistant by subsequent treatment in high-pressure steam (60–80 lb./in.^{2}), or they may be "filled" with lanoline, paraffin, linseed oil, or sealed by treatment in potassium dichromate or sodium silicate.

Of the three processes, the chromic acid method probably gives the best protection for unalloyed aluminium and most alloys low in copper; for alloys with more than 5% copper, the sulphuric or oxalic acid methods should be used.

Magnesium Alloys. Various pretreatment processes giving visible films on which protective paints can be applied have been worked out by Sutton and Le Brocq.[132] Some of the earlier processes involved lengthy dipping, but a 45-minutes dip in a bath containing potassium and ammonium dichromate, ammonium sulphate and ammonia gives an excellent film, which is best covered with paints pigmented with chromates. Another simpler bath much used contains potassium dichromate and nitric acid (sometimes with added nitrates), which considerably improves the resistance to sea water but confers little advantage if the alloys are merely to withstand fresh water. Another mixture contains chromic acid and sulphuric acid.

Bengough and Whitby [9] have produced a selenium coat on magnesium alloys by dipping in a bath containing selenious acid and sodium chloride. The coating is to some extent self-healing ; if a scratch is made on it, the hydrogen selenide produced by decomposition of magnesium selenide deposits fresh selenium on the metal exposed.

Certain magnesium alloys, treated with superheated steam at 200–280° C. for 1–1½ hours, acquire a film which improves performance when painted.

CHAPTER VII

PREVENTION OF CORROSION BY PROTECTIVE COVERINGS

Production of Coverings on Metals

General. The covering used to protect a metal may consist o another metal ; more often it is formed of compounds, organic or inorganic or aggregates of such compounds ; each type of coating may be produced in more than one way.

Metallic Coverings. A layer of a relatively fusible metal may b obtained by *dipping* the article to be coated (previously cleaned by pickling in the molten metal, usually covered with a layer of some flux capable o removing the last trace of oxide from the article. Sometimes specia treatment may be needed ; thus in one process for coating steel strip o wire with aluminium, the steel is passed in turn through hydrochloric acid, boric acid and hydrogen at 900–1000° C., before entering the molten aluminium. In coating steel sheets with zinc, ammonium chloride i placed on molten zinc which produces a layer of molten flux probably containing $ZnCl_2.NH_3$ along with free $ZnCl_2$ and NH_4Cl.

In most cases, the layer produced on steel dipped in molten metal i complex ; on the outside, there may be relatively pure metal, with one or more alloy layers below. In the case of zinc-coated iron, the inne alloy layer is brittle ; it can be made thin by shortening the time during which the iron is kept in the zinc, but this increases the risk of spots failing to receive adequate covering. On tin-coated iron, the alloy layer is usually thin, even if no special precautions are taken ; it is best seen on obliquely cut sections.

The thin tin coats obtained by hot-dipping are apt to contain pores, exposing the steel ; the number of pores decreases as the thickness increases. The places where the iron is exposed can be shown by placing the sheet in water of high purity, heated to 95–100° C. for 3–6 hours, which gives an adherent rust spot at each hole ; another method consists in applying wet paper containing potassium ferricyanide and sodium chloride, which shows up discontinuities as blue points. In the tinning of copper, tin refuses to wet oxide inclusions, which thus become the sites of discontinuities ; copper used for tinning should be free from such inclusions.

Molten lead—if pure—refuses to produce a coat on iron, but if it contains tin, adhesion occurs ; steel coated with lead containing 15–25% of tin is known as *Terne Plate*. Alternatively, adhesion can be obtained if the iron is immersed in antimony chloride solution, to precipitate antimony by simple replacement, and then passed into molten lead or lead-antimony alloy.

Coatings of fusible metals can also be obtained by *spraying* ; an engineering structure can thus be covered after assemblage. The surface is shot-blasted and the metal applied as a shower of tiny globules (often molten), which on striking the surface flatten to give a scaly porous coating.* The spray of globules is obtained from a " pistol " which is moved over the surface. In one form, the metal enters the pistol as wire which is fed forward into a special blow-flame, so that the tip is molten, providing the cloud of droplets which is expelled from the nozzle. In alternative types of pistols, the metal is introduced in the already molten condition or as metallic powder.[127]

Where the articles to be coated are small enough, they can be *electroplated* by cathodic treatment in a solution containing a compound of the metal to be deposited. Many metals do not give a continuous deposit from a solution of a simple salt. Thus silver deposited from a silver nitrate solution consists of a limited number of distinct crystals, but that obtained from a cyanide solution (such as $K[Ag(CN)_2]$ or $Na[Ag(CN)_2]$) is fine—almost structureless—for reasons suggested on p. xxxi. Silver anodes are employed, and, provided that the bath contains excess of free KCN or NaCN, the attack on the anode compensates for loss of silver at the cathode ; if excess of cyanide is not present, deposits may appear on the anode, and attack may be obstructed.

Complex cyanide solutions are also used in the deposition of gold, cadmium, indium and of alloys such as brass. In plating copper upon steel, deposition is often started from a cyanide bath ; if a sulphate bath was used at the outset, incoherent copper would be thrown down by simple replacement. After a thin deposit of cyanide copper has been formed, deposition is usually continued from a copper sulphate bath, containing an addition agent such as gelatin, to improve the deposit, since from such a bath a higher current density (and hence more rapid deposition) is possible.

Zinc is deposited from a cyanide bath if the articles are irregular, on account of the good " throwing power " (p. xxxiii). For less complicated shapes, baths of zinc sulphate containing sodium acetate and gum, glucose or β-naphthol may be used. Similarly, tin, which may be deposited from a complex salt solution (sodium or potassium stannate) when high throwing power is needed, can for general purposes be deposited from a simple sulphate bath containing certain organic mixtures, such as crude cresol-sulphonic acid, lysalbic acid and β-naphthol. Lead can be deposited from a fluoborate or fluosilicate bath with colloid additions. In all these cases, the organic substances added serve to prevent coarse crystalline growths, either by adsorption on the growing crystal, or by forming alternate layers rich and poor in colloid, which keep the deposit smooth and bright.

Other complex salts used in plating include the nitrites. Palladium and rhodium are both deposited from a complex nitrite bath.

Nickel, on the other hand, is an example (p. xxxiii) of a metal which can be deposited as a smooth coherent coating from a simple nickel sulphate solution, without organic additions; boric acid may be adde to control the p_H value, and either nickel or sodium chloride to preven passivity of the nickel anode. For hard deposits, a solution of doubl ammonium nickel sulphate, which possibly contains complex ions, i preferred. Chromium is deposited from a bath made from chromic aci and sulphuric acid (which becomes chromic acid and chromium sulphate) the actual production of metal appears to take place within a thin fil of chromium chromate, which may act rather in the same way as an organi addition agent, producing a bright, almost structureless, metallic deposit

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* The porosity is no great disadvantage if the coating is anodic to the basis metal (see p. 158).

Certain alloy coats can be obtained by *cementation*. Steel article packed in zinc dust with some zinc oxide and heated at 380–450° C. (o in the case of springs as low as 250° C.) become covered with a zinc-iro alloy layer, possessing protective properties; the process is calle *Sherardizing*. Similarly, if steel articles are heated in aluminium powde alumina and ammonium chloride, a layer of iron-aluminium alloy i formed (p. 19); this is the basis of the *Calorizing* process.

Inorganic Coats. Iron may be coated with *Glassy enamel* by applying to the pickled surface powdered glass of suitable composition, ofte suspended in liquid, such as water or turpentine; the articles, after bein dried in warm air, are heated strongly so as to melt the glass, which under suitable conditions, flows over the whole surface producing coherent coat. In general, several coats are applied, the bottom on being chosen for adhesion and the outer ones with a view to resistin corrosion or abrasion—according to the conditions of service envisaged The composition for general purposes is a boro-silicate glass containin fluorine and often lead; it is generally made from borax, felspar, quart and cryolite. For acid-resistance, silica may be increased and titani introduced. Tin oxide or zirconia (introduced as silicate) serve to giv opacity; antimony oxide, which is sometimes used for that purpose, ma be dangerous in vessels intended for foodstuffs. The lowest coat usuall contains compounds of cobalt or nickel which improve the adhesion; is generally believed that a cobalt and nickel tree is formed on the iro by simple replacement, and provides keying. The coefficient of expansio of acid-proof enamels is considerably lower than that of iron, the discrepancy being greater for sheet than for cast iron; it is best to us enamel of high coefficient for the lowest coat, building up with successiv coats of increasing acid-resistance and decreasing coefficient. Defects i enamel coats (chipping, blistering and fish-scaling) were once attribute to oxides of carbon, but are believed to be largely due to the evolutio of hydrogen, which may enter the metal by the action of moistu long before enamelling, but is evolved during the production of th enamel coat.

Thick linings of glass are sometimes used in steel vessels, but a naturally brittle. Cement or concrete layers can be cast in contact wit the metal, and are applied internally and externally to pipes; thinn layers can be obtained with a paint or slurry of Portland cement an water, often containing a little glue.

Organic Coats. Many mixtures containing pitches, tars or bitumens are known which are solid at ordinary temperatures but melt on gentle heating. These can be brushed on when molten, solidifying when cool; thicker coats can be cast or pressed in the plastic state on to the steel, as in the external protection of pipes; for pipe interiors, a centrifugal application gives a smooth, mirror-like surface which facilitates water flow.

Other materials are known which are liquid at ordinary temperatures but become solid when heated, because the molecules can join up to form a three-dimensional network, thus losing their translatory motion. Many of the synthetic resins have this power of thermo-hardening, and form the basis of modern stoving varnishes, or (if they contain pigments) stoving paints. The compositions are often sprayed on the articles, which are then heated in a box-oven, or, more conveniently, exposed to a radiant heat lamp; the exterior layer is then preferentially heated and becomes covered with a tough, adherent coat.

Where heating is inconvenient, a coat may be applied which dries by evaporation. It is common practice to use a solution of some bituminous or resinous substance in a volatile solvent, with or without the admixture of a powdery solid or pigment, which leaves a continuous solid film when the solvent evaporates. Solutions of pitch, tar or bitumen, which dry by evaporation, leave coats possessing considerable protective properties in themselves; they also form a suitable basis on which thicker and more protective coats of similar substances can be applied molten, as suggested above, thus obtaining better adhesion than if the hot coats were applied direct to the metal.

Many paints which dry by evaporation contain resins or other plastics. Solutions of cellulose derivatives with pigments form the basis of cellulose paints. Special importance attaches to solutions of chlorinated rubber or polystyrene, pigmented with zinc dust, since, as explained on p. 159, these produce on steel what is practically a continuous zinc coating in contact with the steel, having much of the protective power of galvanized iron, although they can be applied in the field. Chlorinated rubber and polystyrene paints containing iron oxide, zinc oxide or other pigments possess valuable properties, whilst a clear polystyrene solution without pigment is useful in certain situations.

Most lacquers and paints which dry by evaporation require, in addition to the volatile solvent, a non-volatile organic liquid to act as *plasticizer*; in the absence of such a compound, the films would become brittle and porous when the volatile liquid has evaporated. A plasticizer should be non-volatile, chemically stable, insoluble in water and possess lubricating properties; its rôle seems to be to fill voids in the molecular lattice and provide planes of easy glide. Useful plasticizers include dibutyl phthalate, dibutyl tartrate, ethyl stearate and tricresyl phosphate.

In other cases, the setting of a coat depends less on evaporation than oxidation. The drying paints are among the oldest but most complicated types of covering. They are based on drying oils, which consist of mixtures of glycerides of unsaturated fatty acids. These can take up oxygen at the double bonds, and the oxidized molecules link up together yielding a three-dimensional network, so that the liquid becomes solid; the oxidation and polymerization is favoured by compounds of metals which exist in two stages of oxidation, and can absorb oxygen from the air, passing it on to the oil. Such compounds are known as *driers*, and they may consist of salts of acids (such as linoleic) present as glycerides in the drying oil. In practice compounds of more than one metal are used, and it is not uncommon to find the linoleates of lead, manganese and cobalt in a single paint.

An ordinary oil paint has at least four constituents: the pigment (such as iron oxide, red lead, zinc oxide, zinc chromate, or a mixture of these), the drying oil (linseed, tung, perilla, oiticica or dehydrated castor oil), a drier (linoleate or naphthenate of lead, manganese and/or cobalt) and a thinner (white spirit, a substance resembling petrol but boiling at a higher temperature, or alternatively turpentine). Often a resinous substance (either a natural resin or an oil-soluble synthetic resin) is added, and sometimes other substances, such as the calcium soaps of the acids of drying oils, which confer water resistance. When the paint is spread out on the metal, the thinner soon evaporates, the drier takes up oxygen and passes it on to the drying oil, the molecules of which link up, giving a solid film of pigment particles set in a matrix of the "dried" oil.

Usually drying oils receive refining or heat-treatment before being used in paint. The refining aims at the removal of objectionable minor constituents, particularly the slimy bodies known as "foots", but the heat-treatment modifies the glycerides themselves. The products may be "boiled oil" (obtained by heating with driers), "blown oil" (prepared on passing air through the hot oil) or "stand oil" (made by prolonged heating with exclusion of air and without driers); "stand oil" is particularly valuable, since small quantities added to other oils give paint coats possessing great toughness.

These various paints can be applied by *brushing*, or more quickly by *spraying*. The consistency needed for spraying is thinner than that for brushing; the health hazard may be greater unless precautions are adopted, and there is considered to be more danger of shutting moisture into pores or crevices (in applying a paint by brush much of the water on the surface is expelled and emulsified into the coat). On the other hand, spraying can reach parts of a complex metal structure which might escape brushing.[55]

Mechanism of Protection by Coatings

General. It is still widely believed that coatings prevent attack on the metal covered simply by excluding the corrosive agency, whether gas or liquid. This is often the main—sometimes the sole—cause of protection. However, coatings are known which afford protection notwithstanding that they either consist of a material which is *per se* porous or contain discrete pin-holes, cracks or other discontinuities. Protection of the basis metal exposed at a discontinuity can occur in two separate ways. If the coating contains an inhibitive pigment—such as zinc chromate, this can inhibit in a manner similar to potassium chromate (p. 128), but, being less soluble, is only slowly removed from the coat; other inhibitive pigments, such as red lead, are known, and are discussed on p. 160. A second mode of protection at gaps occurs where the coating is a metal anodic to the basis metal; thus coatings of metallic zinc or aluminium will protect steel even if the latter is exposed at a discontinuity, since in the cell zinc | liquid | steel, or aluminium | liquid | steel, the steel is usually the cathode, and escapes attack, whilst the zinc or aluminium, being the anode, is "sacrificed" in protecting the steel. (Protection by paint coats richly pigmented with metallic zinc is discussed on p. 159; similar paints containing aluminium do not appear to afford cathodic protection at gaps.)

In the paragraphs that follow, it will be assumed that iron or steel constitutes the basis metal to be protected, unless otherwise stated.

Behaviour at a Discontinuity.[37] If steel carrying a discontinuous coating is placed in a natural water, without stirring, the rust, which requires oxygen for its formation, is usually thrown down outside the gap in the coat, and is quite loose. Being very voluminous, it may cover up the coating, but, until so much metal has been destroyed as to undermine the coating between the discontinuities, the coating will remain undamaged in its original situation. With coatings of flaky metal, as obtained from a spraying pistol (or even paints pigmented with flaky metallic particles), the flakes will remain, clinging at certain points to the metal, even after much corrosion has taken place. If the water is in motion, so that there is ready replenishment of oxygen, the rust will be formed close to the metal, and is more likely to seal the discontinuities and stop attack. The presence of calcium salts in the water aids the formation of adherent rust (p. 130), and a hard water will sometimes seal pin-holes in a coat by means of rust blobs, where a sodium chloride solution would cause continuous attack, with the formation of loose rust outside the coat. Finally, if the specimen, instead of being immersed, is exposed to damp, corrosive air (e.g. air with salt spray suspended in it), the rust is formed at each discontinuity below the coating, and, owing to its large volume, may push the coat outwards as a pimple or blister, unless the adhesion is unusually good, in which case the opening will be sealed and corrosion will cease.

This might seem to indicate that atmospheric exposure is more likely to damage the coating than conditions of immersion. But partial immersion in salt water, or the presence of a drop of salt water lodged on a surface in a position where it does not quickly evaporate, may be very destructive to a paint coat; for the alkali formed at the cathodic zone situated at the water-line, or around the periphery of the drop, may act on the paint, softening the vehicle (unless it is alkali-resistant), or may creep between metal and coating, loosening the latter; the actual corrosion of the metal in the anodic zone is generally far less destructive to the coat, although sooner or later undermining will occur if attack continues. "Alkaline softening" is a very serious feature of corrosion of painted metal by salt water.[40] When the coating has locally become loosened, the alkali, which, for electrochemical reasons,* is produced below the film at a concentration exceeding that of the salt water outside, sometimes draws in water by osmosis, and the coating is then pushed outwards as a *blister*. (At anodic points, the film is not loosened, and an adherent nodule of rust appears, partly outside the paint film.)

On iron, alkaline softening and alkaline blistering will only give trouble under the rather exceptional circumstances where alkali accumulates at one place. It is brought about by partial immersion in stagnant salt water, or by the presence of a single drop of salt water lodging at a point where evaporation is slow. It would not be produced by a shower of salt droplets falling on a surface at random. On magnesium, however, the corrosion product will be an alkaline substance (magnesium hydroxide) even in absence of salt, and loosening is more likely. This is probably the main reason why inhibitive pretreatment of magnesium alloys (p. 150) is so necessary if paint is to adhere.

Cathodic or Anodic Coats. If the coating is a metal, or even a paint richly pigmented with a metal, the occurrences will vary greatly according as the coating is cathodic or anodic to the basis metal. On steel, coatings of copper or nickel will normally be cathodic, whereas coatings of zinc and (unalloyed) aluminium will usually be anodic. A cathodic coating will not prevent rusting if there are pin-holes or cracks in it. Indeed, if the coated steel is immersed in a strongly saline (and therefore highly conducting) water, the combination of large cathode and small anode may make the attack at the gap locally more intense than if the steel had been left uncoated. This intensification of attack on steel is more probable at gaps in copper than in nickel coats, owing to the higher E.M.F. It becomes less likely as the conductivity of the water diminishes. In atmospheric attack, with only condensed water or raindrops wetting the coated steel, the attack at a gap is usually *less* intense than that which would take place if the steel was uncovered. A cycle handle-bar, badly plated with nickel, resists the rain better than an unplated one, although clearly worse than one which has been properly covered.

On the other hand, a coating of zinc or aluminium can protect steel exposed at gaps in the coat, provided that the current density upon the steel is sufficient. The coating is destroyed in conferring the protection, but, since the corrosion of the coating must spread sideways, and that of

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* The rate of production of alkali at a point below the paint by the equation

$$O + H_2O + 2e = 2(OH)'$$

is the equivalent of the current flowing from that point. If the current were entirely carried through the electrolyte by anions, the rate of removal would also be the equivalent of the current and no accumulation of OH′ would occur ; but if *part* is carried by cations, a steady increase of (OH)′ ions must take place until a concentration is reached at which it is balanced by (1) diffusion of (OH)′ outwards through the film, (2) the *osmotic* imbibition of water. If the film were adherent, only (1) would occur, but if the alkali has loosened the film, (2) is also possible, and to accommodate the water drawn in, the film must be pushed outwards as a blister. An alternative explanation attributes the blistering to *endosmotic* movement of water towards the cathode.

uncoated steel would at least partly extend downwards, the former is the lesser of two evils; however, when the gap in the coat has been sufficiently enlarged by the corrosion process, the current density in the centre of the gap will cease to be adequate and attack on the steel will start. For that reason, it is important to choose a metal for the coating which will be corroded only just fast enough to confer protection. The choice will depend on the corrosive environment. In some experiments carried out by the author,[37] steel carrying discontinuous aluminium or zinc coatings was tested in salt solution and in a hard water rich in calcium bicarbonate; in such cases aluminium, used as anode, generally gives less current than zinc, owing to the oxide film on the former. In salt solution, both metals afforded cathodic protection to the exposed steel, but, since the zinc delivered more current than the aluminium, it was destroyed more quickly, and rusting started first on the zinc-coated specimens. In the hard water (essentially calcium bicarbonate solution) which was less corrosive, the aluminium was attacked too slowly to provide sufficient current density for protection, and the steel suffered rusting from the outset. Thus the aluminium-coated specimens, which escaped rusting for a long time in the more corrosive liquid, developed rust quickly in the less corrosive.

Paints containing metallic zinc powder in sufficient quantity for the pigment particles to be in contact with one another, and with the steel basis, can confer cathodic protection on exposed steel. Mayne [106] has found that, in order to obtain assurance of protection, the paint coat should (after drying) contain about 95% of zinc. In linseed paints this cannot be obtained without producing a mixture too stiff for easy application. In the case of paints consisting of zinc dust in either polystyrene or chlorinated rubber solution, the required zinc content can be obtained without making the paint unbrushable.

In Mayne's tests plates of steel coated with zinc-rich paint, pierced by a scratch-line, and placed in sea water, remained two years without the formation of loose rust by attack on the exposed steel. Electrical tests indicated that in the early stages the zinc was in connection with the steel, which received cathodic protection. Later, however, the electrical connection ceased (probably because the lowest portions of the zinc had become destroyed through anodic attack); yet protection still continued, probably because, in the earlier stages (when the current was still flowing), zinc hydroxide, calcium carbonate or other compound had been deposited on the exposed steel, as cathodic product. After electrical contact disappeared, any iron compounds formed at the scratch-line may perhaps convert the substance in question into a clinging form of rust; this *clinging* rust could actually be seen, and the fact that no *loose* rust appeared in the liquid indicated that it was really protective.

These zinc-rich paints[50] can be applied to rusty steel, and yet still give protection at scratch-lines during protracted immersion in *sea water;* electrical tests indicate that connection is established through the rust, which is probably reduced locally to metallic iron, thus providing a conducting bridge between steel and zinc. For the protection of completely rusty iron against *atmospheric attack*, zinc-rich paints are of little value; but they afford good protection to pickled steel or steel in which the mill-scale is broken up by rust-patches—a condition difficult to protect by ordinary paints; electric connection between steel and zinc-coat is made through the mill-scale.

Inhibitive Pigments in Paints. Certain pigments used in paint confer protection on iron even where it is exposed at a discontinuity; they include red lead, litharge, metallic lead powder and zinc chromate. Some of these substances diminish the corrosion of iron even when no oil is present; thus Lewis [98] found that specimens of unpainted iron shaken in a tube with air and water (or air and a salt solution) suffered far less loss of weight if one of these pigments had been introduced into the tube, although clearly, being merely a loose powder, it could provide no mechanical shielding of the iron surface. He also found that when a scratch-line was made on iron coated with red lead paint and a drop of N/1000 sodium chloride was placed on it, the iron exposed at the scratch suffered no rusting, although parallel experiments with paint pigmented with iron oxide (a pigment lacking inhibitive properties) invariably led to rusting at the scratch-line. There are, of course, limits to the inhibition conferred by red lead. In experiments where concentrated sodium chloride was used, rusting was not prevented.

There is an essential difference between red lead paint, which prevents corrosion by keeping the iron passive, and iron oxide paint, which only protects iron if corrosive influences are excluded by the *paint* film (as opposed to an *invisible* film formed by the action of the pigment upon the metal.) This difference was shown in some outdoor corrosion tests carried out at Cambridge by Britton.[16] In one series, different amounts of thinner were added to the paints, and the iron oxide paints were found to give less and less protection as the thinner content was increased; the red lead paints, on the other hand, continued to give satisfactory protection after large additions of thinner. Another series in which paints made with oils of different qualities were compared showed that iron oxide paints gave worse protection if made from linseed oil containing " foots " than if made from refined oil; on the other hand, in red lead paints, large amounts of foots could be tolerated without loss of protective power, although they led to an unsightly coat.

The cause of the passivity conferred by pigments may be different in different cases. Zinc chromate doubtless behaves much like potassium chromate (p. 128); to introduce potassium chromate into paint would give short-lived protection, because so soluble a substance would quickly be leached out. On the other hand, a chromate of extremely low solubility might fail to provide the necessary concentration of $(CrO_4)''$ ions. A salt of intermediate solubility must be chosen, and zinc chromate seems appropriate for steel; the zinc ion may play a part by inhibiting the cathodic reaction. Strontium chromate has been used in paints for protecting magnesium alloys.

The causes of inhibition by lead pigments have been studied at Cambridge by Mayne,[105] who finds that some samples of metallic lead powder, litharge or red lead, left in contact with distilled water, render it non-rusting to iron. It would seem that the water comes to contain $Pb^{\cdot\cdot}$ and OH' ions after contact with these pigments, so that the agent responsible for passivity could be regarded as lead hydroxide in all three cases. Lead linoleate also renders the water non-rusting and its solution is more stable towards carbon dioxide than lead hydroxide. Certain pigments, like lead basic carbonate (white lead), which do not directly render the water non-rusting, can, when suspended in linseed oil, deprive water of its corrosive power. It would seem that lead hydroxide, lead linoleate or some hydrolysis product is adsorbed at breaks in the oxide film where anodic attack would normally commence. If the water which has been made non-rusting by contact with a lead compound is shaken with iron filings, previously heated in a reducing atmosphere, it loses lead. Thus a lead pigment seems to provide an adsorption inhibitor which blocks the potential starting places of anodic attack.

Effect of Surface Condition on Performance of Coats. Before applying a metallic coating, it is absolutely necessary to remove all scale, rust and grease. The removal of scale and rust by pickling or shot-blasting has been considered on p. 142; grease may be removed by an alkaline bath containing a silicate, phosphate or aluminate; subsequent removal of alkali is important. Alternatively, dipping in an organic solvent, such as naphtha, is often employed. "Vapour-degreasing" is favoured for some purposes; the article is placed in the upper part of a vessel containing boiling trichlorethylene or other grease-solvent below, so that the liquid condensing on the surface drips down and carries off the grease.

Whether the surface should be smooth or rough depends on the nature of the coating contemplated. On a surface intended to receive a bright plating, all roughness should be avoided, and pickling should be conducted with sufficient inhibitor to ensure this, the inhibitor being chosen to avoid leaving organic contamination on the surface. On the other hand, sprayed coatings adhere badly to a smooth surface, and the grain used in the last stage of shot-blasting should be an angular grit chosen to provide dovetailing for the coating.

The removal of mill-scale and rust is also necessary where glassy enamels are to be applied, although one authority recommends that the surface should finally be heated for a few minutes at 760° C. to produce a thin oxide film, intended to prevent the formation of hydrogen by the action of moisture on the metal.

In the application of organic coats, it is possible to quote examples of mill-scale or foundry-scale being left in position—apparently without harm resulting. For instance, cast iron and cast steel are usually painted without removing the scale, which—if free from sulphur—actually increases the protection; similarly the *adherent* portions of the scale on wrought iron can safely be left in position. Even on rolled steel, there is usually no removal of mill-scale if a thick bituminous layer is to be applied, or if the steel is to be buried in cement.

In most other cases, it is advisable to remove scale and rust before paint is applied. The advantage of this course has been proved in tests organized from Cambridge and carried out at stations representing a number of atmospheres, as well as in a more extensive series conducted on large specimens by J. C. Hudson,[89] acting for the Iron and Steel Institute Corrosion Committee. It is also indicated from service inspections; a survey of painted steelwork in Holland made about 1938 suggested that almost all cases of rapid breakdown were due to mill-scale left on the metal. Sometimes the presence of mill-scale may appear advantageous in the early stages; where a poor paint has been applied over scale, it may develop rust stains less quickly than the same paint applied to clean steel, the scale acting as an additional coat. But when the time comes for repainting, it will be found that coats applied over mill-scale are rising from the surface, owing to rust formed below them at breaks in the scale; in such cases, drastic cleaning will be needed to obtain a proper foundation for the new coat, whereas paint applied to clean steel, even after it has become rust-stained, may often remain sufficiently adherent for the new coats to be applied immediately upon it.

There are, however, numerous types of mill-scale which behave differently. In general, high-temperature scale on steel tends to be bluish, whilst low-temperature scale has a red appearance due to powdery ferric oxide, which can be rubbed off revealing dark grey scale (essentially magnetite) below. Steel rolled at high temperatures has a layer of partly decomposed ferrous oxide at the base of the scale (p. 143), and on weathering this suffers oxidation, with volume changes which cause the outer scale to peel off. Low-temperature scale does not weather off so easily—the ferrous layer being usually absent. Thus if it is desired first to remove the scale by weathering (a less reliable method than pickling or shot-blasting—as emphasized by Hudson), and then to apply the paint on the descaled surface, high-temperature scale is preferable. If it is desired to apply the paint outside the scale, steel rolled at a low temperature is better. But it is best of all to remove the scale and rust by shot-blasting, pickling or grinding just before painting is carried out.

There are two separate reasons why mill-scale below paint is dangerous. First, although the scale may appear adherent, it may crack off, carrying the paint with it, if the steel is bent repeatedly to and fro, as may, for instance, happen on ships' plates during a voyage. Secondly, even without bending, there may be serious rising of paint at any places where the scale has become damaged. The dangerous combination of small anode (the exposed steel) and large cathode (the scale-covered areas) leads to intense attack at the breaks of the scale, the fresh rust there formed appears below the paint (under conditions of atmospheric exposure), and, occupying a far larger volume than that of the iron destroyed in producing it, pushes away the paint from the metal, and causes failure. It might be argued that this would be avoided if the scale was really continuous, or the paint absolutely watertight ; but it is doubtful whether—under practical conditions—scale on steelwork ever is free from discontinuities (sometimes invisible), and probably few paint coats are completely impervious.

If the mill-scale has been removed completely—whether by weathering, grinding, chipping, pickling or shot-blasting (see p. 142)—and if the surface has subsequently become covered with rust, the question arises whether paint can safely be applied on rust. Since the main constituent of rust is ferric oxide, a pigment often used in paint, an affirmative answer might be expected. Actually paint can be successfully applied over the rust produced where a drop of distilled water has been placed on steel (previously cleaned by grinding) and allowed to evaporate. But rust formed on exposure to urban atmospheres generally contains ferrous sulphate, usually unevenly distributed. Mayne has found that where paint is applied upon the rust formed on steel exposed out-of-doors at Cambridge, breakdown seems to occur at places where ferrous salts exist, possibly as a result of the cell

Steel | Ferrous Sulphate | Ferric Rust | Steel

The corrosion produces more ferrous salts at the point of anodic attack, so that, once started, the action will stimulate itself. The presence of inhibitive pigments may in such cases be of limited value ; a chromate, for instance, will be destroyed by interaction with ferrous salts at a slight distance from the anodic surface, and will never reach the seat of attack. Thus painting over rust should be avoided, although tests have shown somewhat variable results, doubtless because the ferrous sulphate content has varied with location and weather conditions.

Where complete removal of rust and scale is not possible, flame-cleaning will bring the surface into a condition suitable to receive paint. Oxy-acetylene burners are moved over the surface, and embrittle the mill-scale and rust, which can afterwards be removed with a power-driven wire-brush. A porous oxide film, probably magnetite, is left, to which paint adheres well, particularly if applied whilst the surface is still warm and dry.

Practical Uses of Different Types of Protective Coverings

Tests on Coated Materials. Two series of outdoor tests on iron or steel specimens coated with different protective coverings were mentioned in the preceding section. Numerous others have been conducted ; the extensive tests of the American Society for Testing Materials deserve special mention. Raft and half-tide tests on coated materials have also been organized, to ascertain behaviour under marine conditions. These have furnished much valuable information regarding the relative value of different coatings in protecting iron or steel, but in calculating service lives from the results it must always be remembered that the geometrical simplicity rightly aimed at on the testing station is rarely met with in service at the points most liable to corrosion, such as contacts and crevices. The warning applies still more forcibly to laboratory tests on coated specimens; such tests, although useful in furnishing quick results under controlled conditions, represent a state of affairs very different from those commonly prevailing in service. For studying the physical deterioration of paint coats, painted specimens are exposed in turn to moisture, heat and ultra-violet light; the sprays and lamps designed to provide the moisture, heat and light may be attached to a stand rotating about a vertical axis, the specimens being arranged in a circle around the stand, and facing inwards. However, the lamps used often furnish a different combination of wave-lengths from that provided by sunlight, and the conditions of drying up of the moisture may, in some forms of the test, be different from those arising naturally in service. Nevertheless, by combining the results of field tests and laboratory tests with observation of performance in service, a fair idea has been gained of the practical utility of different protective systems.

Factors Determining Choice. In the sections which follow, an attempt is made to indicate the main uses of different types of coating. Of course the choice of a coating does not depend on protection against corrosion alone. Resistance to abrasion is also important, and here metal coats, especially some of those obtained by electroplating, enjoy an advantage over organic coverings, although certain of the latter—notably the paints used for motor-car bodies—will stand much rough usage. Again methods used for articles completed in a factory will differ from those suitable for a structure sent abroad in parts, to be assembled and erected in a distant spot. In the first case, which applies to motor-cars, metal furniture, and numerous small internal fittings for houses, such as hooks and door handles, either electro-plating or stoving enamels can be applied, whereas in the second case paints which dry by evaporation or oxidation at ordinary temperatures must generally be employed. Frequently, the parts receive one shop coat of paint intended to give temporary protection during conveyance and erection, which is subsequently covered with other coatings designed for permanent protection; it may often be better, however, to provide a coating of zinc by galvanizing in the factory, and to paint this on the site after erection.

Noble Metals. The chemical resistance of the noble metals might seem to recommend them as coatings, but quite apart from their high cost, they are strongly cathodic to iron, so that at any discontinuity intensified attack may be expected. An early attempt made to put gold-plated steel nibs on the market proved disastrous, since the soft gold was rubbed away at the tip, exposing the steel, which suffered rapid wastage. Where cost permits, thick coats which are free from discontinuity can be obtained mechanically. Thus copper-clad steel plates are made by rolling the two metals together, whilst composite wires carrying a steel core and thick copper sheath are manufactured; here the ductility of copper allows of sharp bending without exposing the steel. Brass may be coated mechanically with gold—the product being known as "rolled gold".

Electrodeposition of noble metals is carried out for special purposes.

Electroplated table ware (usually a nickel-copper-zinc alloy plated with silver) is well known, whilst the silver deposits have been used to protect "heavy duty" bearings on aircraft engines from corrosion by oxidized oil. Palladium plating is applied to silver watches and cigarette cases to prevent tarnishing, whilst rhodium plating has become important in connection with reflectors for searchlight purposes or for beacons at air ports.

Brass plating is sometimes applied to steel cartridge cases to prevent corrosion, but another use is to provide a bond for rubber to steel. Rubber itself is a valuable protective coating, but fails to adhere to many metals ; brass is an exception, and a plating of brass will allow an adherent rubber layer to be subsequently applied.

Nickel and Chromium. Nickel deposits covered with a thinner chromium coat are much used for the protection of steel or brass. The nickel protects the steel or brass against corrosion, whilst the chromium protects the nickel from fogging (p. 74) ; the hardness of the chromium is a further asset. Sometimes four coatings are used, consisting respectively of nickel, copper, nickel and chromium ; the advantage of interposing the copper is connected with the low probability that a pin-hole in the nickel will coincide with one in the copper. The thickness varies with the service conditions envisaged. For steel, one British motor firm has adopted the following thicknesses (expressed in thousandths of an inch) : nickel 0·2, copper 0·5, nickel 0·8 and chromium 0·1 ; for brass, two coats suffice, namely nickel 1·0 and chromium 0·1. The use of nickel plating overlaid with a much thinner chromium plating in "modern" furniture and household fittings is well known ; the combination is generally described as "chromium plating".

Polishing costs can be reduced if the nickel is deposited in bright condition, which is usually attained when parallel layers alternately rich and poor in organic matter are present. Some bright-plating baths contain a sulphonic acid, whilst others depend on the deposition of a nickel-cobalt alloy from a solution containing an ammonium salt, a formate and formaldehyde.

Tin. Although used to some extent for covering copper cooking utensils, copper or lead water pipes, and brass condenser tubes, the main use of tin is in the so-called *tinplate* used by canners. This consists of dead-mild steel carrying a tin layer usually 0·0001 to 0·0002 in. thick ; the number of pores per unit area decreases as the thickness increases, but, however pore-free the plate, as manufactured, may be, the tin layer is usually broken during the fabrication of the can. Fortunately, in fruit juice (probably the most corrosive substance which the canner must face), steel is generally cathodic to tin (which forms complex anions with the fruit acids), so that intense attack on the exposed steel does not occur, although the hydrogen evolved at the cathode may distend the can. Except with a few fruits (e.g. bilberries), failure of cans by hydrogen swelling is more frequent than perforation. The composition of the steel is of importance ; copper should be kept high and phosphorus low. Hoar and his colleagues [82] think that insistence on steel with high copper content (0·16–0·21%) and low phosphorus content (0·03–0·045%) should double the expected life of a can made from hot-rolled steel-base. The newer cold-rolled steel-base also provides tinplate of superior quality.

Another possibility is improved lacquering. The primary purpose of lacquering is to avoid discoloration of the fruit, whose anthocyanin constituents can act as hydrogen-acceptors at a cathode and thus change hue. Lacquering prevents this, but the lacquer coats as applied some years ago, instead of preventing the swollen cans rather increased that trouble. To-day improved stoving lacquers, based on synthetic resins (p. 155), are available; by using two coats (the first applied to the flat sheet before the can is "formed", and the second sprayed on to the finished can to repair any cracks produced in forming) the number of swollen cans can be greatly diminished.

In peace-time, tin was usually applied by hot-dipping, but during the war, electroplating, which gives a more uniform coat and thus economizes the valuable tin without increased risk of swelling or severe corrosion, has been largely employed—especially in America. It is not unlikely that this development has come to stay. Another possibility is the use of thin thermally produced coatings, with a further layer of tin electrodeposited upon it, to reduce porosity.

A recent development is the application of a thin electro-deposited tin coating (0·00003 in. thick or even less) on steel before painting, to prevent the under-rusting which would cause disfigurement or even subsequent peeling of the paint coat. At present, phosphate treatment (p. 149) is largely used for that purpose, but a report by Hedges and Jordan [75] seems to suggest that the thin tin coats provide superior protection to that given by phosphate films. It appears possible that thin tin coats may prove extremely important in increasing the lives of paint coats on motor-car bodies, steel window frames, refrigerators, gas and electric fires, water heaters and steel furniture.

Lead. The special value of lead is its resistance to sulphuric acid, and steel sections coated with lead suitable for the construction of pickling tanks are manufactured. Lead coatings are used on metal window frames, whilst roofs of Terne plate (p. 152) are popular on the Continent. Terne plate also finds employment as drums for paints, and cans for petrol; in regions where the native population relies on the refuse dump as the source of its cooking utensils, outbreaks of lead poisoning have resulted therefrom.

Since lead is mildly cathodic to steel under most conditions, a lead coat will not prevent rusting at pin-holes, but it is stated that the corrosion here stifles itself—an occurrence possibly connected with the inhibitive powers of lead compounds (see p. 161); nevertheless the rust spots will cause disfigurement, unless an outer coat of suitable paint is applied to prevent the trouble.

Zinc. Galvanizing has long been used for protecting steel wire, sheets, pipes, tanks and cisterns. Being anodic to steel, zinc will generally give protection at a gap (except in hot water), but it is used up in the process and thus relatively thick coatings are called for, if the protection s to continue. Thick coatings are apt to be brittle, and the exposure of the steel at a crack, even if it does not lead to immediate attack on the steel itself, will accelerate that on the zinc.

Fortunately, brittleness does not depend on thickness alone. The main reason for brittleness in a zinc coat as obtained by passing steel wire through molten zinc is that the basal plane of the crystals, the only one along which gliding can take place, is usually parallel to the surface of the steel, so that, on bending the wire, fracture must occur, since gliding is excluded. In the *Crapo process* an equiaxed structure is obtained, and there is far less brittleness, since a selection of orientations are presented, thus facilitating gliding; the process consists in preheating the wire by passage through molten lead, then through a cyanide flux to carbonize or nitride it superficially so that it galvanizes easily, and finally through molten zinc, from which it should emerge vertically. Lately, there has been a tendency to adopt electrodeposition of zinc on wire, which gives a coating of uniform thickness—an obvious advantage; for a coating which is thick in one place and thin in another will develop rust quickly at the thin places and will be likely to break at the thick ones—thus combining the evils of thinness and thickness.

On corrugated galvanized iron intended for roofing (or for the walls of sheds), the coating should be thick, unless it is merely intended to protect the steel during transit, paint being applied after erection. Paint does not adhere well to a bright zinc coat, and therefore the surface coating should first be roughened before painting, by brushing with a mixture of commercial hydrochloric acid (5 vols.), carbon tetrachloride (5 vols.), toluol (30 vols.) and denaturated alcohol (60 vols.); after drying it should be wiped with a clean rag. Metallic zinc paint has been recommended for painting galvanized iron.

If the galvanized iron is not to be painted, a thick coat is essential, or rust will soon appear, even in country air. Statements have been made that the life of the coat (up to the appearance of rust) is proportionate to the thickness. These are based on the behaviour of specially prepared samples having coats of very uniform thickness exposed under the simplified conditions of the test station, and do not necessarily apply to service conditions on houses or other structures. The lodging of drops at crevices, or drippings from high roofs on to restricted areas of low ones, are factors which may shorten life, but the main reason for the departure from the Law of Proportionality is lack of uniformity in the coating. The author [37] is acquainted with a case of two samples of galvanized iron exposed at different times in the Scilly Isles. One lasted over 15 times as long as the other, but it was certain that the *mean* thickness was not 15 times as great. Apparently both had been prepared by hot-dipping, and the worst one had probably received a thin non-uniform film which at certain places was very thin indeed. For a long life, the iron should carry about 2 oz./sq. ft. of zinc. If hot-galvanized iron carries less than about 0·7 oz./sq. ft. the coating is usually uneven, so that iron with

0·5 oz./sq. ft., which, according to the proportionality rule, should survive a period equal to one quarter of the life given by 2·0 oz./sq. ft., will in practice enjoy a life much shorter than the calculated value. Possibly by electro-deposition, a greater uniformity could be obtained, but at low thicknesses pin-holes must be expected, and under some conditions the exposure of the steel may accelerate attack on the zinc coating.

Similarly for use below water, a thickly zinc-coated steel should generally last longer than a thin one. A greater thickness is desirable for soft waters than for hard, and indeed it is mainly for waters rich in calcium bicarbonate that galvanized iron tanks and cisterns are useful. When fresh, the unalloyed (outer) coating can confer cathodic protection on any exposed steel against cold water; but the alloy coating gives no such cathodic protection, and even for unalloyed zinc the polarity is reversed at high temperatures, so that the steel exposed at cut edges of galvanized iron receives no protection in hot water—as shown by Kenworthy and Smith.[95] Thus in hot-water systems continuity may be more important than thickness—as such. Bonilla [13] states that galvanized hot-water pipes are actually corroded more quickly than black (mill-scale-covered) pipes in hot-water systems, but less quickly in cold systems. The performance of zinc coats on the exterior of buried steel pipes was mentioned on p. 88.

Sherardized coatings (p. 154) are frequently applied to small bolts and similar factory-made articles, and greatly add to the effective life, although, since the layer consists largely of an iron-zinc alloy layer, a yellowish corrosion deposit is formed at an early stage; this does not mean that protection has ceased, and it should be distinguished from the true rust, which appears when corrosion has penetrated to the steel basis.

The coatings discussed above can only be applied at a factory. Zinc-sprayed coatings (p. 152), are suitable for covering a structure after its erection, e.g. in the protection of steel lattice-work masts; they form a good basis for painting.

Aluminium. Encouraging protection has been obtained on steel by shot-blasting, and then spraying with aluminium from a wire pistol, followed by paint. This process was used throughout the war years in the protection of the hydrogen cylinders used for balloon barrages, and, despite the rough usage and adverse climatic conditions to which these cylinders were exposed, it gave excellent protection. Probably the method will be increasingly used in the protection of structural steelwork. Exposure tests organized from Cambridge [16] on sand-blasted steel, coated with aluminium from a wire pistol, showed admirable behaviour in urban, marine, mixed and country atmospheres. Even where no paint had been applied, specimens exposed seven years in London remain free from rust, although the aluminium showed some deterioration; where paint had been applied, the aluminium coating was completely unchanged. In country air, paint keeps its colour better when applied on aluminium than when placed directly on steel.

Cadmium. At one time it was thought that cadmium would largely displace zinc, owing to the deceptively favourable results of certain salt spray tests which failed to represent service conditions. Cadmium coats do, however, appear to possess superiority over zinc coats for articles intended for the tropics, as they give protection under storage conditions of high humidity and high temperature. Cadmium is at best only mildly anodic to steel, and does not usually furnish protection at gaps.

Indium. Certain high-duty bearings used in aircraft, based on cadmium (with either nickel or silver plus copper), are highly susceptible to corrosion by acids present, or formed during service, in lubricating oils. One method of combating the trouble is to deposit indium; on heating, the indium diffuses into the alloy, and increases the corrosion resistance. Steel bearings are often thickly plated with silver, then more thinly plated with lead, followed by indium or tin, which is " infused " into the lead, thus conferring enhanced resistance to the oils.

Glassy Enamels. The most familiar example of protection by glassy enamels is provided by the household utensils used for washing or cooking purposes. The dangers of jagged particles of enamels entering food has diminished owing to increased understanding of the factors which govern adhesion. Special acid-proof enamels are used in many chemical processes, whilst the protection of buried pipes by glassy enamels is a matter receiving attention. The enamels are non-elastic, and more liable to break off if applied to flimsy steel sheet than rigid cast iron—apart from the fact that the discrepancy of coefficients of expansion is greatest in the case of steel.

Stoving Enamels. The use of organic stoving enamels on motor-cars, cycles, metal furniture, typewriters, telephones, scientific instruments and a host of small manufactured articles has already been mentioned. Where special adhesion is required, or where there is danger of under-rusting, steel articles may receive a phosphate pretreatment (p. 149). Stoving enamels are used on light alloys, and here electrochemical pre-treatment (anodizing) for aluminium-base alloys (p. 150), and chemical inhibitive treatment for magnesium-base alloys (p. 150) is generally regarded as essential. In addition inhibitive pigments, such as zinc chromate, are often introduced into the enamel itself. Chromate pigments should be free from chlorides, sulphates and nitrates.

Oil Paints. The paints based on drying oils possess the advantage that they can be applied in the field. The principle to be followed in selecting the painting scheme should be to apply a " priming coat " containing an inhibitive pigment, such as red lead or zinc chromate, and follow it by one or more outer coats chosen to resist abrasion and exclude water, as far as possible; paints of this class are never completely impervious.

Red lead is frequently diluted with red iron oxide or with graphite; one authority considers that red oxide with only 20% red lead constitutes a better, as well as a cheaper, pigment than undiluted red lead. Similarly graphite paint containing red lead is a good inhibitive primer, although a paint containing graphite alone will stimulate attack, since graphite is cathodic to steel. A mixture of red lead and white lead is used successfully for ships' bottoms where red lead alone is unsatisfactory. There are numerous grades of red lead; those containing much free litharge give paints with superior inhibitive properties but inferior keeping power, as compared with paints made from "non-setting red lead", which contains but little free litharge; the litharge interacts with the oil to give plaster-like compounds, and the paint, unless used immediately after mixing, will set in the pot. However, the whole question of the keeping power of red lead paints is complicated, and free fatty acids in the oil may be beneficial in small amounts, but harmful in large quantities; on this point, a paper by Chater [20] deserves study.

Tests indicate that as an inhibitor zinc chromate is not seriously inferior to red lead, and, as regards keeping power, paints containing it are much superior to those made with the more inhibitive types of red lead; in priming coats it is often mixed with a relatively large amount of iron oxide. Zinc oxide (alone or in admixture with iron oxide) possesses inhibitive properties, but it is liable to be dissolved away by acid water, if the latter gains access to it.

Metallic lead pigments provide inhibitive priming paints, probably producing the same anti-corrosive substances as litharge or red lead (p. 161); objection has been raised to lead on the ground that it is cathodic to steel, and Blom has introduced an alloy pigment with 85% lead, 13% antimony and 2% tin, designed to be equipotential to iron.

The outer coats should be as nearly waterproof as possible, so as to prevent the inhibitors of the inner coat being washed away by water or converted into other substances; (red lead, exposed in polluted atmospheres, may change to lead sulphate). Inhibitive pigments are less necessary in the outer coats than in the priming coat, although many authorities recommend that they should be present in both. The waterproof character of outer coats can be improved if pigments of flaky form are employed; when brushed out the flakes lie parallel to the surface and each other; the path which a molecule must follow before it can pass through a film of a given thickness will clearly be longer than if the paint contained roughly spherical pigment particles. Flaky pigments include metallic aluminium, and the form of iron oxide known as *micaceous iron ore* (also as *flaky hæmatite*).

The principle that the *lowest* coat should contain an *inhibitive* pigment (e.g. red lead) and the *outer* coats an inert pigment chosen for its *physical* properties (e.g. iron oxide) is borne out by tests conducted in all parts of the world. As an example may be cited the conclusions drawn from tests of seven years' duration organized from Cambridge and carried out at four stations representing urban, marine, country and mixed atmospheres. These included two-coat and three-coat systems applied to specimens of steel carrying almost unbroken mill-scale and to other specimens of the same steel freed from scale by mechanical grinding on a coarse wheel. The main conclusions were:—

(1) Descaled specimens generally behaved distinctly better than scale-covered specimens, and in no case behaved worse. In fact, the descaled specimens carrying three coats were in perfect condition after seven years in London. The only exception was the specimen carrying three coats of red iron oxide in linseed oil; here there was no inhibitor in the priming coat, and some breakdown had occurred.

(2) Among priming coats tested below iron oxide covering coats, Blom's alloy pigment (p. 170) behaved at least as well as red lead; (when used as a single coat, this alloy paint gave poor protection). The performance of red lead primers was improved by the addition of litharge, although the paint had then to be applied directly after mixing.

(3) Among the covering coats tested, micaceous iron ore behaved rather better than the red form of iron oxide, although the comparison was not a strict one, since the vehicles were different.

(4) The use, in all coats, of a mixture of tung and linseed oils in proportions chosen to balance the expansion attending the setting of tung by the contraction characteristic of linseed oil, gave results superior to those obtained with refined linseed oil alone.

Somewhat similar conclusions emerged from the extensive tests conducted by Hudson for the Iron and Steel Institute Corrosion Committee in all parts of the world, and particularly from a special series carried out by him, in co-operation with Fancutt, at Derby.

Numerous tests—especially those conducted in the United States—prove the advantage of introducing oil-soluble synthetic resins into air-drying paints, especially those intended for use below water. There is some difference of opinion regarding the use of synthetic resins in the inhibitive priming coat, but their value for the outer coats is not seriously contested. In railway work, where paint has to withstand bombardment by grit particles, the presence of stand oil is particularly welcome in imparting toughness to the outer coats, and the value of this ingredient in other situations has been borne out by exposure tests.

In Great Britain, where the atmosphere is often charged with acids from coal smoke and/or salt from the sea, the breakdown of paint most often occurs from below, being due to voluminous rust formed below the coat at pin-holes, or to cathodically formed alkali which softens and loosens the coat. In the tropics, where there is little atmospheric pollution but powerful sunshine, the attack starts from the outside; the light destroys the vehicle, so that the pigment particles can be rubbed off on gentle friction. This phenomenon (not unknown in Britain) is called *chalking*, and white paints are naturally more affected than dark ones, since the light penetrates more deeply. It can largely be overcome by use of flaky aluminium as pigment; the opaque flakes, lying flat, reflect the light and shield the vehicle. Where it is desired to apply a reflecting coat to oil tanks (or any vessel whose contents must be kept as cool as possible under intense sunshine), aluminium paint is, in the end, more satisfactory than paint carrying a white pigment.

Another precaution to be adopted in hot climates is the inclusion of chemicals to prevent moulds and similar growths, which otherwise especially on iron oxide paints, cause trouble. Linseed paints are mor affected than those based on tung oil, and “ foots ” in the oil increase th growth of moulds. Chlorinated phenols are often added as fungicides red lead, chromates and zinc compounds tend to prevent the troubl although zinc oxide is fungistatic rather than fungicidal, preventin growth instead of killing the spores.

Paints Drying by Evaporation. Some of the early types of paint which harden owing to the evaporation of the solvent had little protectiv value, although often giving attractive coatings. Lately several classe possessing great promise have become available, of which *chlorinate* *rubber* paints, already in industrial use, and *polystyrene* paints deserv mention. One of their most valuable properties is their power to tak up a large quantity of zinc powder (p. 158), thus providing in effect a form of galvanizing which can be applied in the field. Chlorinated rubbe paints pigmented with metallic zinc are already largely used for marin purposes, but, like zinc-pigmented polystyrene, they are liable to develo blisters (p. 159); researches are in progress to overcome this objection which for the moment must limit the application of both classes of paints Recent tests of a semi-service character have shown that chlorinate rubber and polystyrene paints containing various pigments can affor useful protection to steel against polluted urban air under sever conditions.

Tar and Bituminous Paints. There are on the market numerou black compositions made from natural bitumen (rich in aliphatic hydrocarbons), and/or from industrial coal tars (rich in aromatic hydrocarbons) In general, they are more sensitive to light than oil paints, easily developing a network of cracks when exposed to the sun; moreover, many of th older compositions provided coatings which were only serviceable ove a narrow temperature range, so that either the coat became brittle an cracked in cold weather, or it became soft and ran in hot weather. Moder research is tending to overcome these disadvantages, and in situation where light and temperature fluctuations are small, they often give bette performance than most other types of paints. Their use on pipes is a example, whilst some tar paints (usually prepared with lime additions t neutralize tar acids) have shown excellent performance at chemical work where oil paints have failed. Another situation where this type of pain has long been used, is for the boot-topping of ships, that is coating th water-line zone alternately exposed to wind and sea; comparative test carried out by the Institution of Civil Engineers have confirmed thei value at that level, although in the fully immersed part, and the superstructure, oil paints seem to provide better service. In almost all situations, coal tar from horizontal retorts gives better results than that from vertical retorts.

Paints of the tar-bitumen class are somewhat susceptible to the condition of the surface to which they are applied, but by emulsifying bitumen in water products may be obtained capable of application to wet surfaces when the water evaporates, continuous coats remain. Moreover, excellent compositions are known containing bitumen and/or tar along with oils, adapted both for air-drying and stoving. Some of the constituents of tars inhibit the oxidation changes responsible for the "drying" of ordinary oil paints, but they allow polymerization processes at high temperatures. One of the earliest forms of stoving enamels was based on this principle. Pipes coated with mixtures of linseed oil and bitumen, and then heated, were found, after thirty-seven years' burial near Pittsburgh, to be in excellent condition.

Chapter VIII

STATISTICAL AND MATHEMATICAL TREATMENT

Foreword

As explained in the Preface (p. vi), this final chapter is more advance than the rest of the book, from which Mathematics has been almos entirely excluded. The subject of Corrosion cannot, however, be full understood without the application of the Principles of Probability, an it is hoped that the reader will not lose heart too readily if he finds th chapter difficult. The neglect of Probability in the curriculum of so man schools and colleges is probably to be regretted on general grounds, sinc there is no branch of Mathematics which has a closer bearing on th problems of everyday life; but however this may be, the subject canno be ignored if Corrosion is to receive serious study. The last four pages dealing with Lateral Extension of Films, are less important than th others, although they serve to show how a Statistical Procedure recentl developed can solve in a few lines problems which would require man pages, if treated by the methods of ordinary mathematics.

Reproducibility

Effect of Border-Line Conditions. It is well known that frequentl two identical corrosion experiments do not lead to the same result Discrepancy between duplicates is particularly marked when corrosiv solutions have been treated with just enough *deterrent* * to bring them t the border-line of passivity. Near the critical content of deterrent, i is found that some of the specimens remain quite unchanged, wherea others suffer intense local attack. A little thought will indicate that thi lack of reproducibility is inevitable. When no deterrent is present corrosion will start from a large number of centres, but as the deterren concentration is gradually increased the average number of startin points per sq. cm. will steadily diminish. Suppose that the specimen each measure 1 sq. cm., and suppose that the amount of deterrent adde is adjusted so as to make the *average* frequency of starting points equal t 0·5 per sq. cm. It is clear that "perfect reproducibility" would the demand half a starting point per specimen; this is meaningless, and th nearest approach to reproducibility would be obtained with one startin point on half the specimens and none on the rest; in actual practice a few specimens would be found to contain more than one starting point, but whatever the distribution, it is certain that the specimens *cannot* al behave alike.

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[*] A *deterrent* is a chemical which reduces the *probability* of corrosion; an *inhibitor* i a chemical which decreases the *velocity* of corrosion. Many inhibitors are also deterrents but this is not always the case (see p. 25).

Bernouilli's Principle. If the average number of starting points be N per unit area, and the area of a specimen be A, the average number per specimen is AN; this is known as the " expectation ". Even on a big specimen, a count would rarely show exactly AN; some specimens would carry slightly more, others rather fewer. The bigger the specimen, the larger will be the *absolute* deviation from AN commonly met with, but the deviations expressed as *fractions* of the mean value (AN) will become steadily smaller as AN increases, so that the proportionate disparity between duplicate experiments will tend to lessen as the numbers involved become larger.

This is simply an example of a general principle developed towards the end of his life by Daniel Bernouilli (1700–82)—a member of the famous Swiss family of mathematicians. Bernouilli's principle explains why some changes are reproducible and others not. In ordinary chemical reactions, we are dealing with vast numbers of molecules, and if the same experiment is carried out a number of times, the same result—within the limits of observation—will always be obtained. Corrosion changes in an ordinary salt solution, which begin at a large number of points per specimen, and soon spread out until a large fraction of the specimen is suffering fairly uniform attack, are reproducible for the same reason; excellent agreement between duplicate experiments is obtained, provided that the experiments are carried out carefully, and under uniform conditions. It is only when a deterrent is added in amounts sufficient to reduce the number of starting points per specimen to a small number that reproducibility must become poor.

Distributions. A large number of factors may cause the quantitative results of a number of duplicated experiments to be *distributed* about some mean value. One cause of variability is found in the fact that generally metallic materials are not uniform; two specimens cut from the same sheet differ physically or chemically from one another, especially where segregation has occurred in the ingot used in the rolling of that sheet. But even if the material were entirely uniform, error of measurement would still cause a certain " scatter " among the values recorded.

In considering the type of distribution, it is necessary to ask whether continuous or discontinuous variation can take place. If all values between $-\infty$ and $+\infty$ are theoretically possible, including non-integral values, the *Normal Distribution* (see p. 177) is commonly met with; even where negative values would be either impossible or meaningless, the normal law may still express with sufficient accuracy the scatter of observational values immediately around the mean value. If only positive, integral values are possible (e.g. in counting the number of pits on a specimen, where " half-pits " and " minus-pits " would be meaningless), *Poisson's Distribution* (see p. 187) is frequently encountered, provided that events are mutually independent; here the lower limit is zero, but there is no finite upper limit to the values obtainable. A third type, the *Binomial Distribution*, which defines the frequency of occurrence of integral values between zero and a finite upper limit, possesses historical interest to corrosion students, since Tammann's theoretical treatment [136] of the causes of Parting Limits (p. 94) was based on it. It is accorded prominence in books on Statistics, perhaps mainly because the Normal and Poisson Distributions can be derived from it as limiting cases.*

The Binomial Distribution is most simply defined by saying that if an experiment must lead to one of two results, which we may call "success" and "failure" respectively, p being the chance of success and q of failure (so that $p + q = 1$), and if the experiment is repeated m times, the chance of obtaining exactly n failures will be given by the $(n + 1)$th term of the binomial expansion of $(p + q)^m$. For instance, if the experiment is repeated three times, the expansion becomes

$$p^3 + 3p^2q + 3pq^2 + q^3$$

so that the chance of no failures is p^3, that of exactly 1 failure is $3p^2q$, of 2 failures $3pq^2$ and of 3 failures q^3. If m be made very large, so that practically continuous variation becomes possible, and if $p = q = \frac{1}{2}$, a Binomial Distribution approximates in the central part of the series to Normal Distribution. If m is made very large, but p is very small (so that the "expected" number of successes, mp, is still finite), it approximates to the Poisson Distribution.

Distribution Curves. Often, a knowledge of the mean value of a large number of experiments showing a wide scatter is of much smaller practical importance than a distribution curve showing the relative frequency of different values, since such a curve makes it possible to ascertain the probability that a given value will be exceeded. For instance, the average value for the depth of the deepest pit found on each of 1000 pipe sections is of little interest; what is of vital importance is to know on what proportion of the sections the pitting has exceeded a depth equal to the thickness of the pipe. A distribution curve can show this.

Again, it may be desired to know the proportion of articles subjected to corrosion-fatigue which will have lives shorter than a certain duration; a distribution curve can provide that sort of information. Nevertheless the Histogram method of representing distribution often adopted in statistical textbooks is of little value in practical corrosion problems. In that method the articles would be assigned to arbitrary classes according to their lives. Thus all those with lives between 0 and 1 year would form the first class (with mean life 0·5 year), all those with lives between 1 and 2 years the second class (with mean life 1·5 year), and so on; the number in each class would then be plotted against the mean life. Now it is obvious that this method does not make full use of the data, since it is arbitrarily assumed (for instance) that *all* the articles having lives between 1 and 2 years survive for exactly 1·5 year, whereas really their lives are distributed. Furthermore, where the total number of articles is fairly small (less than, say, 100) it is necessary either to make the number of classes small, or to be content with a small number falling within each class; clearly the points cannot be expected to fall well on a curve, and where the total number of articles is still smaller (say, 20), the method becomes unusable.

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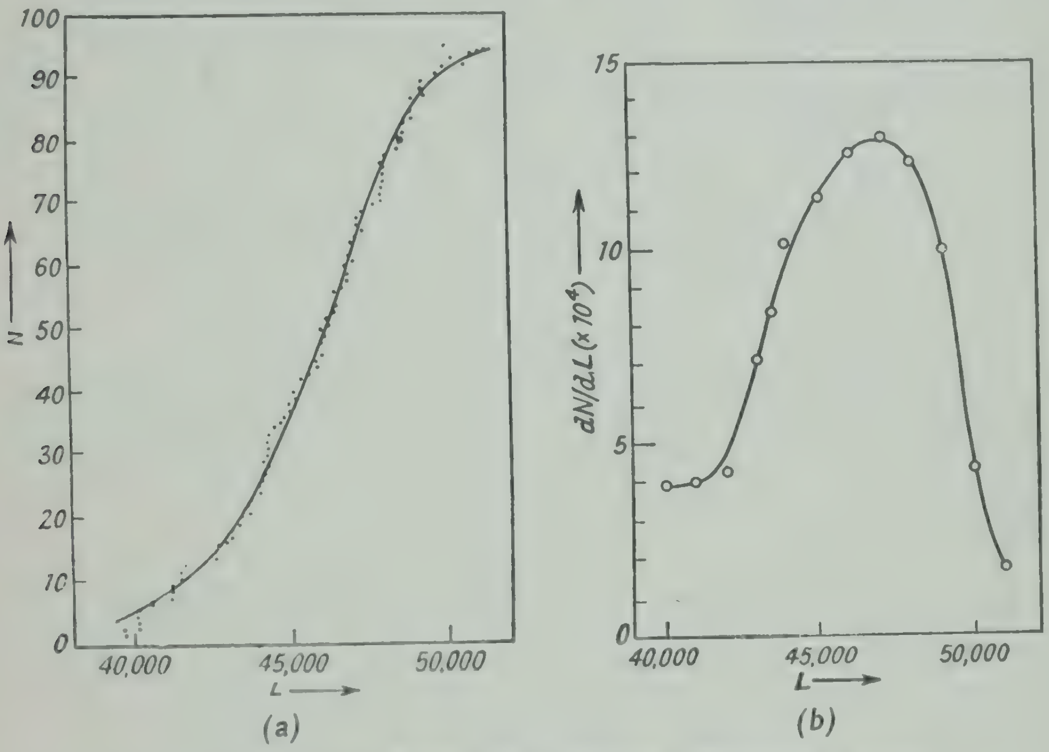
* Actually, in a famous treatise discussing the Probability of a Miscarriage of Justice, published in 1837, Poisson arrived at his distribution as an approximation to the Binomial Distribution under special conditions; but it is unfortunate that statistical writers should so often have adopted the historical derivation since, in the words of Fry, whose book [63] deserves special attention, "there is another point of view which is of much greater practical importance".

In the author's opinion,[45] it is far better to plot, against the life L, the number of articles (N) with lives shorter than L. The number of points available for the curve is then equal to the total number of articles, whereas in the Histogram method it is only equal to the number of classes. Although the points may not fall *exactly* on a curve, the general shape of the graph will not be in doubt even if the number of articles is comparatively small; it will usually be a curve of the form shown in Fig. 62 (*a*) known as an *Ogive*. If it is desired to obtain a curve showing the relative frequency of different lives, this is obtained by differentiation; the plotting of dN/dL against L, using the data of Fig. 62 (*a*), gives the frequency curve shown in Fig. 62 (*b*).



(a) (b)

FIG. 62.—Improved Method of obtaining Frequency Curve.

Experience has shown this method to provide information in an industrial problem where the Histogram method had proved useless.

Normal Distribution

General. If we imagine a vast number of small animals deposited suddenly at a spot on an infinitely long north-south road, and allowed to roam to and fro as they please (keeping to the road), it being supposed that at any moment a given animal is equally likely to move north or south, they will distribute themselves around their starting-point according to the normal law. Errors due to purely *random* causes (as opposed to a definite *bias* tending to produce an error in one direction rather than the other) will usually cause the observations to group themselves symmetrically around the true value as mean, according to the same law. This distribution is commonly defined by the statement that the chance of obtaining a deviation from the mean lying between δ and $\delta + d\delta$ is

$$\frac{e^{-\delta^2/2\sigma^2}}{\sigma\sqrt{2\pi}}\,d\delta \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where σ^2 represents the *variance*, defined as the *mean* value of δ^2 for numerous observations. By converting the law to standardized form, that is by expressing the actual deviation of a particular observation (δ) as a fraction of the *standard deviation* (σ), which is the square root of the variance, a *single* equation can be made to represent *all* normal distributions—irrespective of the absolute value of σ. Thus if τ is written for δ/σ, the distribution can be concisely defined by stating that the chance of obtaining a value between τ and $\tau + d\tau$ is

$$\frac{e^{-\tau^2/2}}{\sqrt{2\pi}}\,d\tau \quad . \quad . \quad . \quad . \quad . \quad (2)$$

The probability of obtaining a given deviation expressed in this standardized manner is always the same. Thus the chance of the deviation exceeding σ is 1 in 3, that of exceeding 2σ is 1 in 20, whilst that of exceeding 3σ is only 1 in 370 ; there is a roughly equal chance of obtaining deviations greater or less than $\frac{2}{3}\sigma$.

Measures of Scatter. The standard deviation, σ, or alternatively its square, the variance, is a convenient indication of the wideness of scatter of observations ; the variance is the simpler conception and has the advantage of being, in certain circumstances, additive (see below).

If we knew the " true value " (which, in the absence of " bias " or systematic error, may be defined as the mean of an infinite number of observations), so that the deviation δ of each measurement from that true value could be written down, then the variance derived from n measurements would be $\frac{1}{n}\Sigma\delta^2$ and the standard deviation $\sigma = \sqrt{\frac{\Sigma\delta^2}{n}}$. In general, however, the true value of the mean is unknown, and the mean of the limited number of measurements performed must be taken as the best available estimate of it ; in such a case, the *best estimate* of the standard deviation can be shown [118] to be $\sqrt{\frac{\Sigma\delta^2}{n-1}}$; this estimated standard deviation is usually written s.

It is common knowledge that, although the mean of a limited number of experiments generally differs from the true value, as defined above, the error involved tends to diminish as the number of experiments performed becomes larger. If a large number of sets, each consisting of n

experiments, were performed, the means of the sets would themselves be spread out around a "master mean"; but they will be clustered more closely than the results within any one set. The standard deviation of the means of the sets (from the master mean) is known as the *standard error* (S_n); it can be shown [12] that the standard error is only $1/\sqrt{n}$ of the standard deviation of the individual measurements, so that

$$S_n = \frac{s}{\sqrt{n}} = \sqrt{\frac{\Sigma\delta^2}{n(n-1)}} \quad . \quad . \quad . \quad . \quad (3)$$

which for large values of n is roughly equal to $\frac{\sqrt{\Sigma\delta^2}}{n}$.

Clearly the *absolute* error ($\varDelta$) of the mean of a set of measurements tells us little; it will look small if small quantities are being measured, and large if large quantities are under review, although it does not follow that less care has been taken to ensure accuracy in the second case. It is more satisfactory to write the error in a standardized form, by expressing it as a fraction of the standard error. The *standardized error* (as the author prefers to call it) is usually denoted by t and is sometimes known as the *t-function*. It is non-dimensional, so that its value is the same whether measurements are made in pounds and feet, or in grams and centimetres. Moreover, for a given type of distribution and a given value of n, the probability of reaching a certain value of t is the same, whatever the *absolute* scatter of the results may be. This valuable statistic can be expressed

$$t = \frac{\varDelta}{S_n} = \frac{\varDelta\sqrt{n}}{s} \quad . \quad . \quad . \quad . \quad (4)$$

where $\varDelta$ is the deviation of the mean of a particular set of n from the true value.

Tests for Efficacy

Effect of a Qualitative Modification.[48] Suppose that it is desired to test the effect of introducing some modification of procedure on corrosion velocity (or corrosion probability) which can either be introduced or omitted but which is not variable in degree. The modification may, for instance, consist in the attachment of a zinc protector strip or other "gadget" (using the word in its widest sense). In such a case, two sets of trials will be made, one employing the gadget (or its equivalent) and the other omitting it, and the results will then be compared.

If all the observed values of efficiency obtained with a gadget lie well above those obtained without it, it is clear that an improvement has been brought about. But supposing, for instance, the values obtained are the following:—

With the gadget	11·8,	10·0,	11·6,	11·8,	average 11·3;
Without the gadget	10·6,	9·8,	9·3,	10·3,	average 10·0.

Here the *average* value obtained with the gadget is greater than that obtained without it, yet two of the individual values obtained without i lie above the lowest value obtained in its presence. The question wil then be asked: is the gadget really beneficial, or is it merely a chanc that the average obtained when it was used lies higher than the other This question is pertinent, since, if two identical sets of experiments ha been performed, both without the gadget, the average values would no in general have been the same. It is clear that, any "positive" differenc between the means found experimentally (i.e. one which seems to indicat the gadget as advantageous) might be attributed to error, and calculatio of the *t*-function enables us to decide what chance there would be o obtaining such a positive difference experimentally, if the accurate valu of the difference were negative, that is if the action of the gadget wer really unfavourable.

Although standard deviations and standard errors cannot be added o subtracted, their *squares* are *additive*; further, the standard error of th *difference* between two quantities, with individual standard errors S_1 an S_2, is the same as the standard error of their *sum*. Thus, in the absenc of correlation between the sets,

$$S^2_{1+2} = S^2_{1-2} = S^2_1 + S^2_2 = \frac{s^2}{n_1} + \frac{s^2}{n_2}$$

where n_1 and n_2 are the numbers in the two sets, whence

$$S_{1+2} = S_{1-2} = s\sqrt{\frac{1}{n_1} + \frac{1}{n_2}} = s\sqrt{\frac{n_1 + n_2}{n_1 n_2}} \quad . \quad . \quad (5$$

assuming the two sets drawn from a homogeneous population, so that a single value of s can be assigned to the whole. Thus the standardize error or *t*-function of the difference between the means of the two set will be

$$t = \frac{\Delta}{S_{1-2}} = \frac{\Delta}{s}\sqrt{\frac{n_1 n_2}{n_1 + n_2}}$$

In the case of two sets s will be

$$\sqrt{\frac{\Sigma\delta_1^2 + \Sigma\delta_2^2}{(n_1 - 1) + (n_2 - 1)}}$$

where δ_1 and δ_2 are the deviations of individual readings from the appropriate means, so that

$$t = \Delta\sqrt{\frac{n_1 n_2(n_1 + n_2 - 2)}{(n_1 + n_2)\ (\Sigma\delta_1^2 + \Sigma\delta_2^2)}} \quad . \quad . \quad . \quad (6)$$

This is the formula commonly used in assessing the significance of the difference between the mean values of the two sets.

It is now possible to consider whether our two sets of numbers really represent evidence that the gadget is effective. Let the "true" effect of the gadget, which would require an infinite number of observations to determine, be a shift $+ x_T$; and let the experimental shift, resulting from the limited number of observations carried out, be $+ x_E$. Now we *know* that x_E is positive, but the numerical value of x_T *might* be negative. The deviation from the true value measured in the positive direction is $x_E - x_T$. Any positive deviation greater than $+ x_E$ means that the value of x_T is really negative, and that the information supplied by the evidence is misleading. The combined chance that a value of x_T which is really negative may nevertheless be producing the positive value of x_E actually obtained is represented by the integral $\int_{t_E}^{\infty} y dt$, where t_E is the value of t obtained from the experimental data by means of expression (6), and y the frequency of different values of t. The values of this integral for different values of N (the total number of observations in the two sets) are indicated by the scale P_t in Fig. 63; they represent the (small) chance that the positive difference obtained by experiment, which seems to indicate that the gadget was acting favourably, could have been reached even though the gadget was—in point of fact—exerting an *unfavourable* influence.*

Taking as an example the two sets of numbers quoted above (obtained with and without the gadget), it will be found that $\Delta = 1{\cdot}3$, $n_1 = 4$, $n_2 = 4$, and calculation from formula (6) shows that $t_E = 2{\cdot}5$. The curves of Fig. 63 show that the value of the integral for $t_E = 2{\cdot}5$, $N = 8$ is only about 0·023, or 1 in 43. The fact that the tentative hypothesis (that a positive value of x_E represents a negative value of x_T) has led to an improbable conclusion suggests that the hypothesis was wrong, and that the gadget is, in fact, producing a genuine *improvement* in the results; this answers the question of efficacy—in so far as it can be answered by so small a number of experiments.

It should, however, be understood that anyone who spends his life in testing gadgets by means of sets of eight experiments must, if he "passes" a gadget as effective whenever the t-value is found to be equal to or greater than 2·5, expect to be wrong sometimes. Opinion differs as to the value of P_t below which the "hypothesis" may be rejected and the improvement regarded as "proven". Some authorities put the limit at 0·05, but others demand a figure as low as 0·01 before they pass the difference between the sets as "significant".

Clearly, the choice can never be purely objective. It will depend on temperament; the cautious man, who is loath to admit the "effectiveness" of the gadget whilst there is even a small chance that its apparent influence can be attributed to the "play of chance", will reject the gadget at values of P_t which the more credulous would accept as evidence of effectiveness. But the choice must also depend on whether there are *a priori* reasons for, or against, the view that the gadget is effective; if assumption of its effectiveness would seem inconsistent with principles which have been vindicated by experience in innumerable other cases

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* The scale P_S, equal to $1 - P_t$, represents the values furnished by "Student's" Tables, which are reproduced in Yule and Kendall's book.[165] The scale P_F gives the doubled numbers presented in the tables of Fisher's book [59]; these do not appear directly applicable to our present problem.

It is, of course, purely a matter of convenience whether curves or tables are used; provided that the numbers are accurately extracted, the result should be the same in each case.

(if, for instance, the claims made for it appear to run counter to the Law of Thermodynamics), there will be a justifiable reluctance to adopt th view that it is functioning, even if t is high and P_t low. Statistics offe no dispensation from the use of common sense.

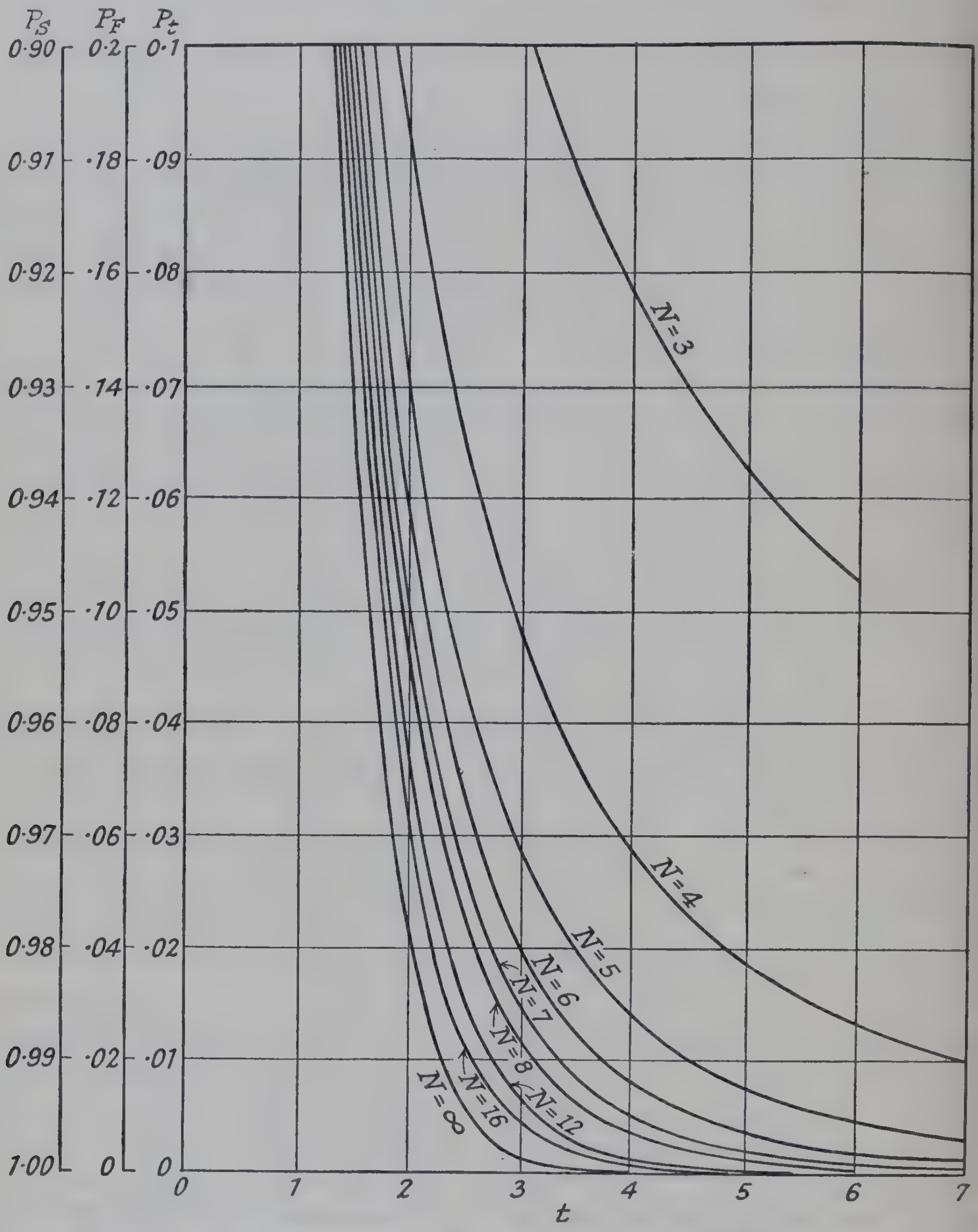

FIG. 63.—The Probability of exceeding Different Values of t when the True Value is Zero (R. S. Thornhill).

The expression used in calculating P_t, namely

$$P_t = \int_{t_E}^{\infty} y\,dt = \int_{t_E}^{\infty} y_0 \Big/ \left(1 + \frac{t^2}{\nu}\right)^{\frac{\nu+1}{2}} dt,$$ where ν represents the Degrees of Freedom and $y = y_0$ when $t = 0$, tends towards the probability integral

of normal distribution $y_0\int_{t_E}^{\infty} e^{-t^2/2}\,dt$ as ν becomes large, so that P_t becomes independent of ν and therefore of N, although N is used, of course, in calculating t. (For small values of ν, y_0 depends on ν).

Effect of a Quantitative Modification. In many cases, a modification can be introduced in varying degree. Thus minor constituents such as sulphur or copper may be present in steel in varying amounts, and their result on corrosion velocity (or corrosion probability) may be adverse or favourable. Suppose that the corrosion velocities of a series of steels differing in sulphur content and in other respects are measured, and that there is a general tendency for the corrosion to be faster when sulphur is high, although when corrosion velocity is plotted against sulphur content, the points do not fall on a curve, owing to the influence of other physical or chemical differences in the various steels. The question then arises: is this tendency for corrosion velocity to rise with sulphur content a sign that sulphur is a dangerous constituent of steel (or is associated with some other constituent directly dangerous to steel), or should it be attributed to the play of chance?

To solve such problems, use is made of another statistic, generally denoted by r, and called the *Correlation Coefficient.* It may be defined as the difference between the means of the products and the products of the means, divided by the two standard deviations—thus

$$r_{ab} = \frac{M_{ab} - M_a M_b}{s_a s_b} \quad . \quad . \quad . \quad . \quad (7)$$

where M is the mean of the quantity suffixed, and the suffixes (a) and (b) represent the factors whose possible correlation is under examination; in our example, (a) may represent the sulphur content and (b) the corrosion velocity. If (a) has no influence on (b), there is no reason why the means of the products should differ from the products of the means, and r will be zero. If, however, high values of (a) tend to produce high values of (b), the mean of the products will exceed the products of the means, and r will have a positive value, although it can never exceed $+1$, which represents perfect positive correlation. If (b) tends to decline as (a) rises, the correlation coefficient will be negative, but can never fall below -1. If the value of r be high (approaching $+1$) or low (approaching -1), this constitutes evidence that the element under study is a genuine stimulator or a genuine inhibitor. But—as in the case of t—there is the possibility that, even in cases where the true value of r (based on an infinite number of experiments) would be negative, a positive value may be furnished by the finite set of tests actually carried out. It is necessary to know the chance that in such cases the experimental value of r could have been furnished from a true value of opposite sign. The appropriate probability integrals (P_r) are plotted in Fig. 64.

Table XVII, based on Mears's measurements,[107] shows the effect of various elements present in steel on the proportion of drops (of area 1 × 1 mm.) which develop rust, when allowed to act on steel for twenty-two hours. The results indicate that sulphur has an adverse effect, but tha copper is favourable, doubtless because it "fixes" sulphur as stabl copper sulphide.

An example may be given of a correlation coefficient leading th unwary astray. Supposing that two elements, say sulphur and phos phorus, tend to be segregated in a certain part of a steel ingot, and tha an experimenter measures (1) the phosphorus content and (2) the corrosio velocity of samples from different parts of the ingot; after calculating and finding it to be high, he reaches the conclusion that a high phosphoru content "causes" high corrosion velocity. This conclusion, however, not necessarily correct, because it may be the sulphur content (which generally high at places where the phosphorus content is high) tha causes the high corrosion velocity of certain parts. It is misleading t say that a high value of r shows that phosphorus *causes* rapid corrosion

TABLE XVII

Correlation Coefficients of Corrosion-Probability (R. B. Mears)

	French Emery Finish	Lathe-Turned Finish
Carbon	+ 0·45	+ 0·26
Sulphur	+ 0·52	+ 0·54
Manganese	+ 0·32	+ 0·47
Silicon	+ 0·19	− 0·13
Phosphorus	− 0·02	− 0·20
Copper	− 0·12	− 0·38

but in cases where a high correlation coefficient is found between phos phorus and corrosion, it is perfectly reasonable to regard a high phosphoru content of any particular sample as a warning that the corrosion is likel to be high, even if this is only due to the association of phosphorus wit another element (sulphur), which—in the case under consideration—*doe* stimulate corrosion.

The fact that a high positive value of the (total) correlation coefficien may appear to attribute to an element a danger which is really due t some second factor with which the element tends to be associated is no a fatal objection to the use of the method. To the practical user of steel it matters little whether phosphorus is the immediate cause of corrosion, o whether it is merely a danger-signal of the presence of some other facto which directly causes corrosion; in either case, a high phosphorus conten in a material—in the absence of other evidence—should cause the materia to be regarded as suspect. To the scientist, however, it is desirable t distinguish between direct and indirect effects, and here the partia correlation method may be of service.

The *total* correlation coefficient used above denotes the correlatio between the corrosion velocity (or corrosion probability) and the conten

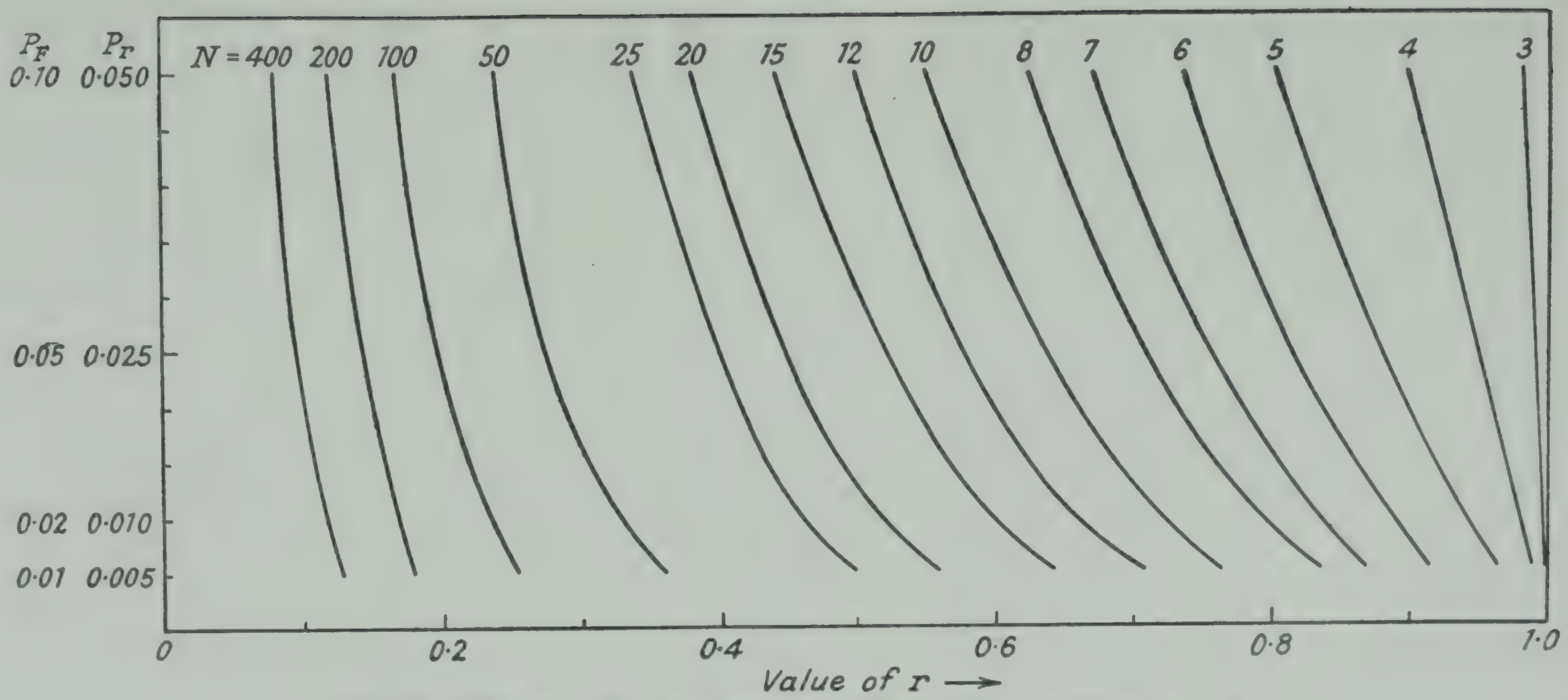

FIG. 64.—The Probability of exceeding Different Values of r when the True Value is Zero (R. S. Thornhill).

of some particular element when the contents of all the others are allowe to *roam* freely in a manner representative of the population of material under consideration. The *Partial Correlation Coefficient* denotes th correlation when one or more of the other factors are held constant. Th partial correlation between factors 1 and 2, with a factor 3 held constant may be written

$$(r_{12})_3 = \frac{r_{12} - r_{13}r_{23}}{\sqrt{(1 - r_{13}^2)\ (1 - r_{23}^2)}} \qquad . \quad . \quad . \quad (8$$

From this *first-order* partial correlation it is possible to obtain a *secon order* partial correlation, in which a fourth variable is restrained fro roaming :—

$$(r_{12})_{34} = \frac{(r_{12})_4 - (r_{13})_4\ (r_{23})_4}{\sqrt{(1 - (r_{13})_4^2)\ (1 - (r_{23})_4^2)}} \qquad . \quad . \quad . \quad (9$$

An excellent example of the use of the Partial Correlation method i provided by Hoar and Havenhand's data [81] for the effect of sulphu phosphorus and copper on the velocity of corrosion of dead mild stee by citric acid. The various correlation coefficients are reproduced i Table XVIII.

TABLE XVIII

CORRELATION COEFFICIENTS (T. P. Hoar and D. Havenhand)

Total Correlation Coefficients	First-Order Partial Correlation Coefficients	Second-Order Partial Correlation Coefficients
$r_{S\rho} = +\ 0{\cdot}20$	$(r_{S\rho})_{Cu} = +\ 0{\cdot}85$ $(r_{S\rho})_{P} = -\ 0{\cdot}03$	$(r_{S\rho})_{Cu,\ P} = +\ 0{\cdot}79$
$r_{P\rho} = +\ 0{\cdot}28$	$(r_{P\rho})_{Cu} = +\ 0{\cdot}59$ $(r_{P\rho})_{S} = +\ 0{\cdot}19$	$(r_{P\rho})_{Cu,\ S} = -\ 0{\cdot}34$
$r_{Cu\rho} = -\ 0{\cdot}51$	$(r_{Cu\rho})_{S} = -\ 0{\cdot}89$ $(r_{Cu\rho})_{P} = -\ 0{\cdot}69$	$r(_{Cu\rho})_{S,\ P} = -\ 0{\cdot}90$
$r_{SP} = +\ 0{\cdot}81$ $r_{Cu \cdot S} = +\ 0{\cdot}66$ $r_{Cu \cdot P} = -\ 0{\cdot}37$		

Here the suffix ρ represents the corrosion velocity. The negativ value of the correlation coefficient $r_{Cu\rho}$ indicates that, when all elemen are roaming freely, the corrosion velocity diminishes with increasin copper content, whilst the positive values of $r_{S\rho}$ and $r_{P\rho}$ show that it ten to increase with increasing sulphur and phosphorus content ; but, sin the positive value of r_{SP} shows that high sulphur contents are associate with high phosphorus contents, it remains uncertain which of the elements is the real stimulator of corrosion. The situation is furth complicated by the fact that the positive value of $r_{Cu,\,S}$ shows that hig copper contents tend to go with high sulphur contents. For this reaso it is necessary to calculate second-order partial coefficients, in which tw of the three elements are prevented from roaming. It is then seen that the large positive value of $(r_{S_P})_{Cu,P}$ indicates definitely that sulphur is *per se* a stimulator of corrosion. The high negative value of $(r_{Cu,P})_{SP}$ shows that, under conditions of constant sulphur and phosphorus content, copper is definitely an inhibitor of corrosion. Calculations of significance show that these conclusions regarding sulphur and copper can be accepted *unreservedly*, for the particular conditions in question, although other conditions are known where sulphur has little effect on corrosion, whilst phosphorus is distinctly dangerous (p. 165).

The Poisson Distribution

Probability and Expectation. On p. 174 it was pointed out that on a number of specimens subjected to a corrosive liquid containing a deterrent, the number of starting points of attack may vary slightly from specimen to specimen. If we define the " expectation " (E) as the average number per specimen obtained after counts on an infinite number of specimens, then under ideal conditions the probability of obtaining n points of attack on any specimen would be given by *Poisson's formula*

$$\frac{e^{-\mathrm{E}}\mathrm{E}^n}{\underline{\lvert n}} \quad . \quad . \quad . \quad . \quad . \ (10)$$

The conditions for validity demand that the occurrence of one point of attack shall not influence the chance of the inception of attack at points around it. In practice, these conditions are not fulfilled. One point may often " protect " the area around, reducing the chance of inception of attack. Alternatively corrosion products from the first point, settling on other uncorroded points, may " infect " these points (e.g. by screening them from deterrent), thus increasing the chance of corrosion. In such circumstances, Poisson's expression, at least for the higher values of n, cannot be expected to express the state of affairs, and it is not surprising that Mears and Brown [108] have found that the distribution of pits on aluminium is not that predicted by the Poisson formula.

In one case, however, the probability is accurately represented by that formula, namely when $n = 0$, since the disturbances due to protection or infection will then be absent. Since $e^0 = 1$ and $\underline{\lvert 0} = 1$, it follows that the chance of obtaining no attack is $e^{-\mathrm{E}}$. It is important to note that here E represents the number which *would* be expected if there were no protection or infection, and is best obtained by considering the chance of occurrence on an infinitesimal area, so that the chance of two breakdowns on the area can be neglected. Let the chance of breakdown on $d\mathrm{A}$ be *defined* as $pd\mathrm{A}$, then the value (E) of the expected number of points of attack on the finite area A to be used in Poisson's formula will be $p\mathrm{A}$. Thus the chance that the area A will *escape* attack will be $e^{-p\mathrm{A}}$, and the chance of getting one or more points of attack is $1 - e^{-p\mathrm{A}}$. This relation between specimen size and probability of attack is represented graphically in Fig. 65, curve (1).

Effect of Deterrents. Supposing now that a deterrent is present which depresses the probability on dA from pdA to pdA/j, then clearl the chance of one or more points of attack becomes $1 - e^{-pA/j}$, an in order to obtain any specified probability value, we require a specime j times as large as in the absence of deterrents. The curves 2, 3 and on Fig. 65 correspond to $j = 2$, $j = 3$ and $j = 4$, and may be regarde as representing increasing concentrations of the same deterrent, or alterna tively a series of deterrents of increasing power. It will be evident tha attack becomes practically certain—however powerful the deterrent— the specimen is sufficiently large.

Utility of Deterrents. The curves of Fig. 65 make it clear that th presence of a substance which is a deterrent but not an inhibitor will b

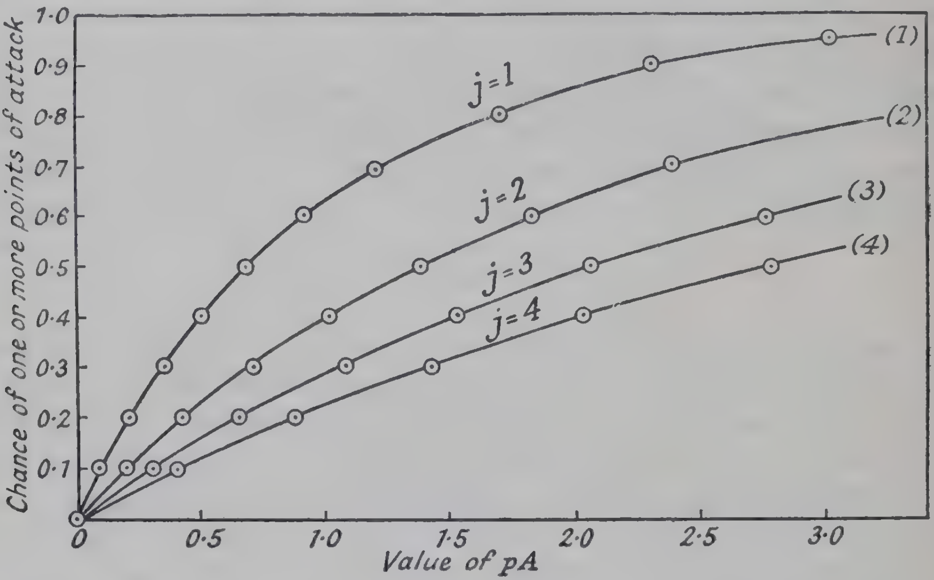

FIG. 65.—Dependence of Chance of Attack on Specimen Area.

most useful when the area exposed is small, e.g. at a pin-hole in a pr tective coat. Where the area is very large, the probability becom nearly unity, whether a deterrent is present or not. On the other han a chemical which is both a deterrent and an inhibitor of the "safe" cla (p. 135) is always worth adding, since on small areas it diminishes th danger of attack occurring at all, and in any event reduces the intensit which may be anticipated if attack does set in; the pigment, red lead- much used in paints—seems to possess under many conditions th desirable combination of properties.

It may be asked whether there is ever an advantage in having prese a deterrent which is not an inhibitor, even in cases where the aggrega area exposed is so large that attack is practically certain to set in som where, notwithstanding the presence of the deterrent. Consider the ca of a large sheet coated with a paint containing so many pin-holes th attack is inevitable. By adding a deterrent the expected number points of attack may be reduced to $1/j$ of the former value. Will th diminish the time needed for perforation of the sheet? The answer that, where the metal and the conditions are so uniform that the conditional velocity at all points is the same, there may be little advantage in reducing the number of points of attack, if the time of perforation alone is under consideration. (Obviously the rate of leakage of water through the perforated sheet, or the volume of rust sludge produced, will, other things being equal, be diminished by the deterrent.) But, if the conditional velocity is not the same at all points, then the larger the number of points where attack develops, the greater the risk of including among them a point of exceptionally rapid corrosion velocity (e.g. at a sulphur segregate). The wider the spread of the frequency curve representing the distribution of different values of conditional velocity, the greater will be the benefits conferred by a deterrent in lengthening the expected time needed for perforation.

Chance of Perforation. Since inhibitors sometimes tend to localize corrosion and increase the chance of perforating a plate, pipe or tank, there is interest in calculating the probability of attaining the depth needed for perforation within a certain time. Obviously this will increase with the area under consideration. If the probability of *attaining* the depth needed for perforation within standard time on an infinitesimal area dA be denoted by pdA, the chance that a finite area A shall *escape* perforation in that time will be e^{-pA}, provided that the pits at different points are considered to have no influence on one another (this will become approximately true when they are far apart); otherwise the expression needs modification, but in all cases the risk of obtaining at least one perforation must increase with the area under consideration. Measurements of pits on buried pipe specimens have shown that this is, indeed, the case.

Maximum Depth of Penetration as Criterion of Damage. For many practical purposes, the depth of the deepest pit (or deepest depression caused by corrosion) is a better criterion of damage than the loss of weight, which represents the total destruction of metal (see p. 76). But for the reasons just explained, the maximum depth of penetration is *meaningless unless the area is stated.* Even if the area is defined, duplicate experiments may show considerable variation in the maximum depth measured, for the following reason. The distribution curve showing the *average* number of pits or depressions exceeding any given depth (D) occurring on each specimen plotted against D, if based on study of an infinite number of specimens, will be a *smooth* curve (Fig. 66 (A)), but the curve of the *actual* depths corresponding to a *single* (finite) specimen must be a *stepped* curve (Fig. 66 (B)), the last step corresponding to the deepest pit (or depression), the penultimate step to the deepest but one, and so on. Obviously if the various stepped curves of an infinite number of finite specimens are combined, they must blend into the smooth curve; but this can only happen if the steps on the various individual curves occur at different places, which means that the maximum depth of penetration, as represented by the last step, will, in general, be different on different specimens.

Actually, considerable variation is often noticed between maximum depths when corrosion is highly localized. The fact that sometimes the reproducibility is fairly good even in such cases may be connected with the form of the distribution curve. If there is some limiting velocity o penetration which, on chemical or electrochemical grounds, can *never b exceeded* at any point, however favourably situated it be for intensifie

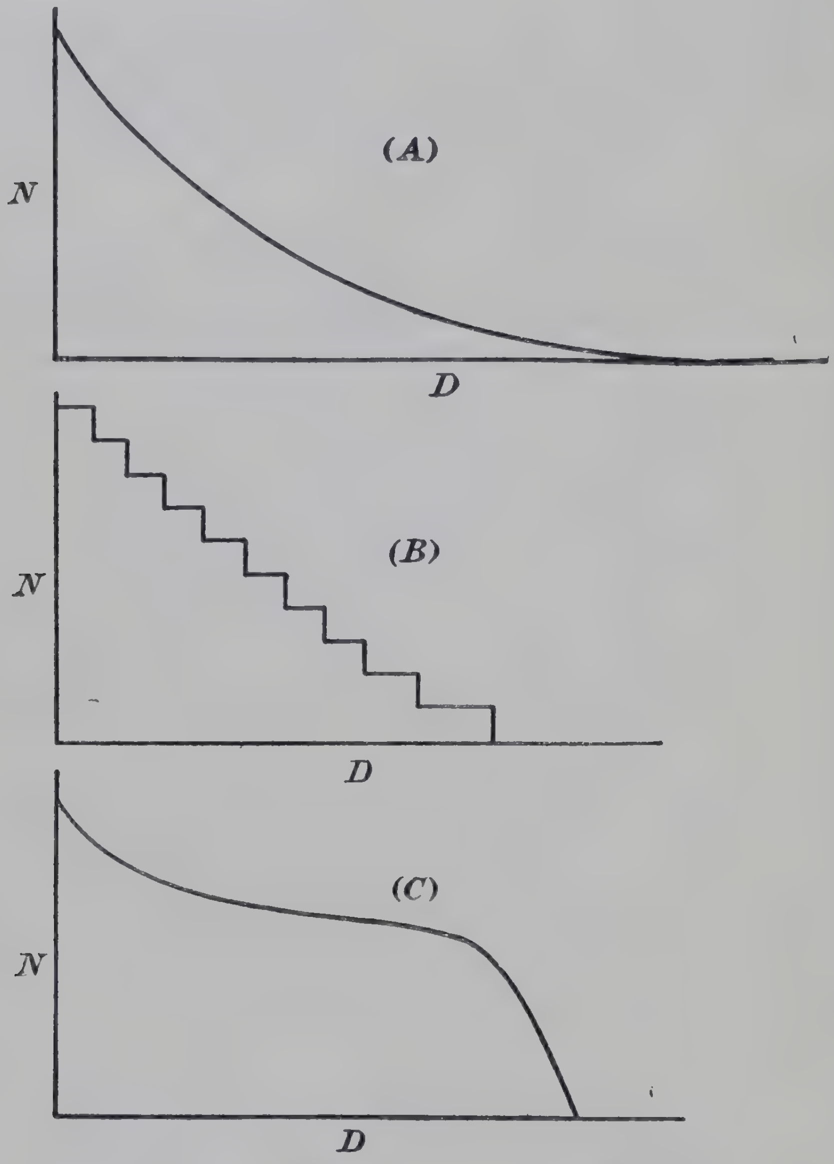

FIG. 66.—Distribution of Depths of Penetration.

attack, the distribution curve must be one which will *cut* the D-axi (Fig. 66 (C)) instead of becoming asymptotic to it, as on Fig. 66 (A) In such a case, a little consideration will show that, provided the specimen are big enough to ensure that at least one depression on each closel approaches the maximum depth obtainable within the time, reproducibility should become good.

The Laws Governing the Thickening of Films

General. Film thickening may occur by passage of material through the lattice itself or through discrete cracks. Metal is more likely to pass outwards through the lattice than non-metal inwards, since in most oxides and analogous compounds the cationic radius is smaller than the anionic radius; such movement is, however, only probable where the lattice is a faulty one—which may, for instance, occur if there is departure from the composition expressed by the formula of the film substance; moreover, the movement of cations must be accompanied by movement of electrons, and compounds of theoretical composition possess, in general, poor conductivity. Outward movement might perhaps occur along grain boundaries, where the structure is loosened, quite apart from any question of composition. Where passage takes place through wide cracks or pores, oxygen will probably pass inwards more easily than metal outwards.

Film-Growth dependent on Lattice Migration. At a temperature range high enough both to avoid cracking, and to allow passage through the lattice itself, it is reasonable to expect that, whatever the exact mechanism, the rate of passage will be inversely proportional to thickness. Thus

$$dy/dt = \mathrm{k}/y \quad . \quad . \quad . \quad . \quad . \quad (11)$$

where k is a constant. Integration gives

$$y^2 = \mathrm{K}_1 t + \mathrm{K}_2 \quad . \quad . \quad . \quad . \quad (12)$$

where the constant K_1 represents $2k$. This parabolic equation is found to govern the oxidation of many metals—copper, iron, cobalt, nickel and tungsten—at high temperatures, but K_1 varies greatly from metal to metal, and clearly the mechanism demands consideration in greater detail.

The fact that film substances of high electrical resistance generally confer good resistance to oxidation, suggests an electrical transport, and Wagner,[160] Hoar,[83] Price and Thomas [123] have ascribed film growth to the movement of cations and electrons from the metal through the film substance to the outside of the film, where oxygen atoms await them; thus the film extends outwards, as indicated by Pfeil.[119] The transport can be regarded as a current I (in amperes) equal, by Ohm's law, to $\mathrm{E}/(\mathrm{R}_e + \mathrm{R}_i)$, where E is the E.M.F. in volts of the cell Metal | Oxygen (or Metal) | Non-Metal, whilst R_e and R_i are the resistances in ohms towards electrons and ions respectively. These resistances must be *added* to give the total resistance, since they are really *in series*; if the flow of either ions *or* electrons were prevented, all passage would cease, just as in a primary cell with a metallic wire joining the terminals, current would cease if the wire were cut, or if the jar were emptied of electrolyte; the fact that during oxidation ions and electrons both flow through the same film does not affect the additive character of the resistances.

The specific conductivity (κ) of the film substance is defined as the current which will flow across a cube of edge-length 1 cm. when 1 volt is applied to opposite faces. Now, in the general case, the movement of electrons, cations and anions may all contribute to the current, in proportions represented by three transport numbers n_e, n_c and n_a, where $n_e + n_c + n_a = 1$. Thus the specific *electronic* conductivity of the material is $n_e\kappa$ and the specific *ionic* conductivity $(n_c + n_a)\kappa$. The electronic resistance (R_e ohms) of a film of area A sq. cm., and thickness y cm. will be $y/An_e\kappa$, and the ionic resistance (R_i) will be

$$\frac{y}{A(n_c + n_a)\kappa}$$

Thus
$$R_e + R_i = \frac{y}{A\kappa}\left(\frac{1}{n_e} + \frac{1}{n_c + n_a}\right) = \frac{y}{A\kappa n_e(n_c + n_a)}$$

since $n_e + n_c + n_a = 1$

Now by Faraday's law

$$dy/dt = JI/AFD$$

where J is the equivalent weight of the film substance, D its density, and F Faraday's number. Again, by Ohm's law

$$I = \frac{E}{R_e + R_i} = \frac{EA\kappa n_e(n_c + n_a)}{y}$$

Hence

$$dy/dt = \frac{J\kappa n_e(n_c + n_a)E}{DF}\cdot\frac{1}{y} \quad . \quad . \quad . \quad (13)$$

Comparing this with

$$dy/dt = k/y$$

it is clear that we have a means of obtaining k, and hence K_1 (which is $2k$) from the electrical properties of the film substance, and the free energy of formation of the oxide, which is ZEF where Z is the valency of the metal. The proof just given is essentially that developed by Hoar and Price, although the equation had been developed previously by Wagner without using the concept of the electrolytic cell.

It has been assumed above that the conductivity is not seriously influenced by the partial pressure of oxygen. If this is not the case, a more general relationship can be reached. It can be shown, from the law of mass action, that the conductivity at pressure P can be written $\kappa_P = \kappa_1 P^x$. Then if the equilibrium oxygen pressure corresponding to the compositions at the outer and inner faces of the film be P_o and P_i respectively, it can be shown that

$$\frac{dy}{dt} = \frac{J\kappa_1 n_e(n_c + n_a)}{yDF}\cdot\frac{RT}{xzF}(P_o^x - P_i^x) \quad . \quad . \quad (14)$$

where R is the gas constant, T the absolute temperature, and z the "valency factor", i.e. the valency multiplied by the number of atoms in the molecule (for oxygen, $z = 4$).

Unfortunately, there are comparatively few cases where the values of the conductivity and transport numbers are known. Three of these cases, comprising the formation of oxide, sulphide and iodide films respectively, are collected in Table XIX, and it is seen that the calculated and experimental values of K′ (which is equal to Dk/J) are always of the same order of magnitude, and the agreement as close as can be expected.

TABLE XIX

CALCULATED AND EXPERIMENTAL VALUES OF THE CONSTANT K′ AS DEFINED BY THE EQUATION $d\eta/dt = K'/y$, WHERE η IS THE AMOUNT OF OXIDE, SULPHIDE OR IODIDE IN EQUIVALENTS PER SQ. CM.

(Tabulated by L. E. Price[122] from papers by C. Wagner)

Reaction	Temperature	Calculated	Experimental
$2Cu + I_2 = 2CuI$	195° C.	$3{\cdot}8 \times 10^{-10}$	$3{\cdot}4 \times 10^{-10}$
$4Cu + O_2 = 2Cu_2O$	1000° C.	6×10^{-9}	7×10^{-9}
$2Ag + S = \alpha Ag_2S$	220° C.	2 to 4×10^{-6}	$1{\cdot}6 \times 10^{-6}$

Still more interesting is the case of copper-aluminium alloys (see p. 21). Here the transport numbers are not known, but the value of $n_e(n_c + n_a)$ cannot exceed 0·25 if $n_e + n_c + n_a$ is to be unity. Assuming this value (the most unfavourable for protection), the presence of aluminium in copper should increase the protection 80,000 times. Since Fröhlich only obtained an increase of 36 times, it is clear that either the electrical theory is wrong, or that the film contains copper. By using their method of Selective Oxidation to obtain an invisible film of alumina free from copper, Price and Thomas [123] actually obtained a great increase of protection, which, assuming the validity of the law $dy/dt = k/y$, worked out at 200,000 times. Although the validity of that law in the case of an alumina film may be doubted, the protection was certainly of the order of magnitude to be expected from the theory, which thus received further confirmation.

Influence of Temperature on Growth-Rate. In all cases of movement through a film, the diffusing particles, whether atoms or ions, have to move in jumps from one position of low potential energy to the next. In general, a particle will only be able to make this move if it attains the requisite energy. The number of particles which possess a critical energy equal to or greater than E is proportional to $e^{-E/RT}$. Thus in the case of a metal obeying the parabolic law

$$dy/dt = k/y$$

k will be proportional to $e^{-E/RT}$; in other words a straight line should be obtained on plotting $\log k$ against $1/T$. Such a relation has been found for copper and brass by Vernon [148] and Dunn [32]; on iron, Portevin and his colleagues [121] found two curves intersecting at about 930° C., apparently owing to the $\alpha \rightleftharpoons \gamma$ transformation.

Hoar points out that the exponential relation between oxidation velocity and temperature follows immediately from the electrical conception of film growth. The conductivity of the film depends on the number of lattice defects and their mobility, and since both these things vary exponentially with the inverse of the temperature, it follows that the velocity constant, which is proportional to the conductivity, will vary exponentially also.

Although, in general, the oxidation velocity falls off rapidly as temperature is lowered, according to the law suggested above, complications must arise when the temperature becomes so reduced that the film, being no longer plastic, begins to develop cracks.

Pores or Cracks in Films. If, as on light metals, the oxide or other compound occupies a smaller volume than that of the metal destroyed, a porous film may be expected, and is observed; if, as on heavy metals, it occupies a larger volume, the film is likely to be in lateral compression, and cracking becomes possible in the temperature range where the film substance is brittle. Electron diffraction research [56] suggests that this compression really exists. Again when oxide films (within certain ranges of thickness) are loosened by anodic undermining of the metal, the film wrinkles up,[54a] indicating that it was previously under lateral constraint. A film attached to a metal basis is like a compressed spring; any cracking of the film liberates part of the internal energy of compression around the crack, and such cracks do, in fact, arise.

The effect of infrequent cracking is well illustrated by the early work of Pilling and Bedworth on copper at 500° C. and that of Vernon on aluminium at ordinary temperature (pp. 13, 14). Here sudden cracking in the film causes the corrosion rate, previously slow, to rise again; the behaviour of aluminium is particularly instructive, since, but for the sudden rises due to cracking, the oxidation would soon become negligibly slow; possibly, as suggested by Mott,[114] an alumina film cannot thicken sensibly beyond the thickness at which electron-penetration by the tunnel effect becomes sluggish. In both these examples, however, we are dealing with infrequent crackings of a catastrophic character, which give rise to a break in the curves, so that no one simple equation can adequately represent the relation between thickness (y) and time (t).

If, however, instead of a few catastrophic cracks, we are dealing with a succession of minor cracks, a smooth curve may be expected, but it is likely to obey a different equation from that which would control the situation in the absence of cracking.

Film Growth dependent on repeated Mechanical Breakdown.[46] If the film substance is under compressional stress, some form of mechanical collapse must be expected, unless the temperature is sufficiently high for a "smooth" rearrangement of atoms by recrystallization or otherwise. If the cohesion of the film substance is weak and its adhesion to the metal strong, collapse may take the form of a series of *shear-cracks*, which will rarely be broad enough to admit oxygen to the metal; generally they will favour outward movement of cations by migration along the walls of the cracks, so that parabolic growth can proceed at an enhanced rate.

If cohesion is good but adhesion at certain points poor, the film may rise at these points as *blisters*. The walls of the blisters are themselves likely to be cracked, and if the cracks are large enough to admit oxygen to the cavity within a blister, the metal at its base should suffer fresh oxidation. In general, we may expect a fresh blister to rise whenever the thickness of the film growing at the base of a previous blister has reached a value y_B such that

$$a y_B Q W_C = a W_A \quad \text{or} \quad y_B = \frac{W_A}{Q W_C}$$

where W_C is the compressional energy per unit *volume*, W_A the adhesional work per unit *area*, a the area affected, and Q the proportion of energy liberated when a blister is formed, which may itself depend upon a. If fresh blistering occurs whenever the thickness reaches y_B, we may expect to get a film of pastry-like structure, with flat cavities lying on different planes, parallel to the surface. Clearly the growth, judged over long periods, should obey a *rectilinear law* $dy/dt = k'$. The rectilinear constant k' should be connected with the parabolic constant k, being equal to $\psi k/Y$, where ψ is the fraction of the area which at any moment is covered by cavities connected by cracks with the outer atmosphere, and $1/Y$ is the *mean* value of $1/y_P$, *averaged over time*, y_P being the thickness of the new (pseudomorphic) film growing at the base of the blister. Now

$$\frac{1}{Y} = \frac{\int \frac{1}{y_P}\,dt}{\int dt} = \frac{\int_0^{y_B} \frac{1}{k}\,dy_P}{\int_0^{y_B} \frac{y_P}{k}\,dy_P} = \frac{2}{y_B}$$

so that

$$k' = \frac{2\psi Q W_C}{W_A} k$$

If the walls of the blisters are *not* pervious to oxygen, the flat cavities formed by the blistering will constitute barriers to the outward passage of cations, which will be hindered at any point lying immediately below such a barrier. At any point which does not lie immediately below a cavity barrier, the network of minor rifts which probably thread the bridges between the cavities should be helpful to the outward migration of cations, since passage along the walls of a rift can proceed more easily than passage through the crystal-lattice. It is thought that at such points practically the whole resistance to outward migration resides in the basal layer where the lateral compression is still unrelieved, the structure being pseudomorphic after the metal. At a point not situated below a cavity barrier the local velocity of growth should have a value (k'', say), independent of y; but to obtain the average rate of growth over th whole surface, we must multiply by a function of y representing th chance that a typical point may escape being covered by a cavity barrie It is necessary to calculate the probability that a line drawn from th typical point at right angles to the metallic surface may pass through th entire thickness of the film without meeting a cavity barrier, using th argument of p. 187. If the chance of a barrier lying in the element *d* is *defined* as $k'''dy$, the chance that there will be no barrier anywhere o the whole length y is $e^{-k'''y}$, since the "expected number" of barrie crossed is $k'''y$. Consequently the average rate of growth on the whol surface is represented by the equation

$$dy/dt = k''e^{-k'''y}$$

Integration gives $y = \frac{1}{k'''}\log_e(k''k'''t + Ck''')$. Writing K$_3$ for 1k'' K$_4$ for $k''k'''$ and K$_5$ for Ck''', we have

$$y = K_3 \log(K_4t + K_5)$$

It should be noted that k''' (and therefore K$_3$, K$_4$ and K$_5$) must depen in part upon the degree of correlation between the position of the cavit barriers in different layers; k''' is small when they are accurately i register one over the other, and large when their positions have littl relation to one another.

This provides an interpretation of the *logarithmic equation*, whic controls the oxidation of zinc in fairly pure air, and that of iron an copper at relatively low temperatures.

The logarithmic relation could, however, be obtained in the absen of cavity barriers. Any type of obstacle would equally lead to t logarithmic equation, if sporadically dispersed. For instance, if a fil developed pores at right angles to the metallic surface which becam blocked in places through any cause (e.g. through welding-together the walls, or through the formation of new crystals growing right acro the pores, thus interrupting passage), then if the chance of such an obstac occurring in length element *dy* was defined as $k'''dy$, the chance of a give pore penetrating through the whole thickness y would be $e^{-k'''y}$, leadi to the relation

$$dy/dt = k''e^{-k'''y} \text{ or } y = K_3 \log(K_4t + K_5)$$

Other circumstances leading to a logarithmic growth law could suggested.

Laws governing the Lateral Extension of Films

General. The preceding section deals with the growth of film *in depth*; the quantitative laws of thickening have been established experiment, and reasonable interpretations are available. In the openi stages of film growth, however, we may be dealing, not with the thickeni of a uniform film, but with the lateral extension of a film which has start at certain points and is spreading outwards. In his quantitative stu of film-formation on an anode during passivation (p. 40), W. J. Müller indicated that the film in the early stages spread laterally, preserving a fairly uniform thickness, but that when the uncovered area had been reduced to a certain small fraction of the whole, growth in depth started, so that the thickness increased with time, the exposed area remaining practically constant. Lateral growth is also met with in the atmospheric rusting of iron and steel; Vernon [147] noticed that steel exposed to certain atmospheres became covered with moss-like growths, whilst Patterson,[117] studying pure iron, reported extension of rust over the surface from centres as expanding circles.

In the simple combination of metal and oxygen, it seems likely that lateral growth may occur in certain cases. Bangham [4] has recently published experiments carried out by Bloomer as early as 1925, on the oxidation of copper exposed to low pressures of oxygen; these led to sigmoid curves, the oxidation rate increasing with time in the early stages, but falling off again in the later stages. Bangham attributes the results to the infrequency of formation of oxide nuclei; when once a nucleus has been formed, the cuprous oxide phase spreads from it laterally over the surface. Some of Wagner's curves [160] for copper also show sigmoid tendencies.

The subject is complicated, since, when once any point has been reached by the lateral extension, growth in depth will set in there. The complete theoretical treatment of the two forms of growth proceeding simultaneously has not yet been worked out. But, confining himself to the single phenomenon of lateral extension, the author [49] has obtained a theoretical relation between the uncovered fraction (α) of the surface and the time (t). The argument is summarized below:—

Types of Nucleation. If film-formation is to commence at nuclei, there are various possibilities. The nuclei may keep appearing in a random manner on the ever-shrinking uncovered portion in a manner determined by the *Nucleation Rate*, Ω, best defined by stating that the probability of a nucleus being formed in time element dt on area $\delta\alpha$ is $\Omega\delta\alpha dt$. Alternatively, it may be supposed that predetermined nuclei are already present at the outset ($t = 0$), and that growth from each of these starts immediately (no others appearing subsequently); the number of nuclei is then determined by the *nucleation density*, ω, best defined by stating that the probability of a nucleus being present on area $\delta\alpha$ is $\omega\delta\alpha$. In both cases the rate of spreading is determined by the velocity, v, which, in the case of films spreading in circles, represents the rate of growth of the radius, and in the case of films spreading in other forms, represents the Root Mean Square value of that velocity (assessed over all angular directions). There is a third possibility that the chance of any point becoming covered with film is not influenced by the presence of film in the vicinity, i.e. that there is *no nucleation* at all.

The Covering of a Surface by Films Spreading out as Expanding Circles from Nuclei which appear sporadically in Time and Position on the still Uncovered Portion. To understand this case it may be well to bring to mind the familiar sight of raindrops falling sporadically on a puddle. Let it be assumed that the rain begins suddenly at time $t = 0$, producing circles which expand over the surface. Consider the number of circles which pass over some representative point, Q, in time t. Ideally, the chance that this number will be exactly n is given by Poisson's formula $e^{-\mathrm{E}}\mathrm{E}^n/\underline{|n}$, where E is the Expected Number, the value obtained by averaging the counts of an infinite number of showers; this is only true if the distribution of drops is truly random (it would be incorrect near trees or dripping roofs), but the formula is then an exact one.

To obtain E, it is convenient to compute the elementary contribution $d\mathrm{E}$ due to an annulus of breadth dr, situated around Q at radial distance r, and then to integrate for all values of r from zero to vt; clearly nuclei developing at distances exceeding vt cannot reach Q within time t. Integration is permissible, because *Expectation* is additive; often *Probability* is not.

The annulus in question possesses an area $2\pi r dr$, and during a period equal to $(t - r/v)$, any point within the annulus will be capable of sending out circles which will reach Q before time t. Thus

$$d\mathrm{E} = \Omega\left(t - \frac{r}{v}\right).2\pi r dr$$

Consequently

$$\mathrm{E} = 2\pi\Omega\int_0^{vt}(tr - r^2/v)dr = \pi\Omega v^2t^3/3$$

The chance that Q shall *escape* being crossed by any of the expanding circles which started after $t = 0$ will clearly be

$$p_0 = e^{-\mathrm{E}} = e^{-\pi\Omega v^2t^3/3}$$

since both E^0 and $\underline{|0}$ are unity. This formula may be applied to give the value of α, the fraction of an area which remains uncovered by a film after time t, since clearly α is equal to the probability p_0 that a representative point shall remain uncovered.

At first sight the two cases of the expanding circles produced by raindrops and the expanding circles of film-covered area would appear to be different, since, in the case of the raindrops, fresh circles can appear from nuclei situated within circles already formed. Certainly the calculation of the chance that n circles shall cross the representative point is not applicable to the case of film growth; indeed the representative point can only be crossed by one circle. But as regards the special case when $n = 0$, the two problems are identical, since a small (late) circle expanding within a large (early) circle would always reach a point after the large one, and the chance that the representative point shall remain entirely uncovered cannot be affected by the fact that when once a circular area has become covered with film, no further nuclei can form thereon. Thus we can at once write for the film-free area.

$$\alpha = e^{-\mathrm{E}} = e^{-\pi\Omega v^2t^3/3}$$

Expansion shows that at very small values of t, the equation approximates to

$$\alpha = 1 - \pi\Omega v^2 t^3/3$$

so that the curves are clearly **S**-shaped, becoming steeper with time at small values of t, and less steep again as α asymptotically approaches zero.

The Covering of a Surface by Films Spreading out as Expanding Circles from Predetermined Nuclei, distributed sporadically in Position. Here the conception of time does not arise, since all nuclei function from the beginning of exposure, and no new ones subsequently come into operation. The contribution dE of an annulus of radius r and breadth dr is clearly $2\pi r.dr.\omega$, so that

$$E = 2\pi\omega\int_0^{vt} rdr = \pi\omega v^2 t^2$$

and

$$\alpha = e^{-E} = e^{-\pi\omega v^2 t^2}$$

Here again the curves are **S**-shaped, and the opening stage can be approximately represented by

$$\alpha = 1 - \pi\omega v^2 t^2$$

Relations between α and t where there is no Nucleation. In this case, the chance that an area element shall be covered within any time element dt will be proportional to the area still uncovered, so that

$$-d\alpha/dt = k\alpha$$

leading to

$$\alpha = e^{-kt}$$

Comparison between Formulæ. It will be noticed that where there is no nucleation,

the formula for α is e^{-kt}

where there are predetermined nuclei, which start to function at $t = 0$

the formula for α is e^{-kt^2}

where there are nuclei which keep appearing on the uncovered fraction,

the formula for α is e^{-kt^3}

Thus if a relation between α and t could be experimentally determined, it would be possible, by merely finding what power of t would give a straight line when plotted against log α, to obtain valuable information regarding the opening stages of oxidation or other film-forming reaction. This suggests a possibly fruitful line for future work.

Grain Size in a Coat formed by Lateral Extension from Nuclei. It may be occasionally interesting to consider, in the case of a film formed by lateral growth from nuclei, the mean size of the grains which have grown from the different nuclei. In the case of growth from predetermined nuclei, this is clearly equal to $1/\omega$. Where we are dealing with films formed by expansion from nuclei appearing sporadically on the still uncovered portion, the mean grain size can be obtained as follows. The total number of grains per unit area formed throughout the solidification process will be $\int_0^\infty \alpha\Omega dt$, which is equal to $\Omega\int_0^\infty e^{-\pi\Omega v^2 t^3/3}dt$. Writing x for t^3, and a for $\pi v^2\Omega/3$, the integral becomes

$$\frac{\Omega}{3}\int_0^\infty x^{-2/3}e^{-ax}dx = \frac{\Omega}{3}\cdot\frac{\Gamma(1/3)}{\alpha^{1/3}}$$

The mean grain size is then the reciprocal,

$$\frac{3\alpha^{1/3}}{\Omega\Gamma(1/3)} = \frac{\alpha^{1/3}}{\Omega}\cdot\frac{1}{0{\cdot}893} = \frac{\sqrt[3]{\pi v^2\Omega^{-2/3}}}{0{\cdot}893} = 1{\cdot}137\left(\frac{v}{\Omega}\right)^{2/3}$$

This expression may be of interest in connection with the size of the grains or spangles formed in a metallic coat obtained by hot-dipping, but it is only valid if the velocity of outward growth from the nuclei is constant in time, and is not determined by other factors, such as the rate of removal of heat.

In the paper quoted,[49] the author has used the same gamma-function method to calculate the mean volumes of grains in a three-dimensional mass. Provided that v is constant with time, this is found to be $1{\cdot}117\left(\frac{v}{\Omega'}\right)^{3/4}$, where Ω' is defined by stating that the chance of a nucleus appearing in volume δV and time dA is $\Omega'\delta V dA$. But the expression has no direct bearing on ordinary casting conditions, where v is not constant, owing to considerations of interfacial energy and the removal of latent heat. In any case, a discussion of Grain Size in Castings is not a proper subject for a book devoted to the Corrosion of Metals.

For the latest theoretical and experimental information on the subject of film growth, the reader's attention is directed to the papers quoted on p. 25.

LIST OF ABBREVIATIONS

AEHW	*Archiv für das Eisenhüttenwesen.*
BSC	*Bulletin de la Société chimique de France.*
BSJR	*Bureau of Standards Journal of Research.*
CI	*Chemistry and Industry* (Review Section).
CSM	*Carnegie Scholarship Memoirs* (Iron and Steel Institute).
E	*The Engineer.*
GER	*General Electric Review.*
IEC	*Industrial and Engineering Chemistry.*
ISISR	*Iron and Steel Institute Special Reports.*
JACS	*Journal of the American Chemical Society.*
JCS	*Journal of the Chemical Society of London.*
JIM	*Journal of the Institute of Metals.*
JISI	*Journal of the Iron and Steel Institute.*
JOCCA	*Journal of the Oil and Colour Chemists Association.*
JOSA	*Journal of the Optical Society of America.*
JSCI	*Journal of the Society of Chemical Industry.*
JSI	*Journal of Scientific Instruments.*
KM	*Korrosion und Metallschutz.*
KT	*Bericht über die Korrosionstagung.*
MI	*Metal Industry* (London).
MMPA	*Mitteilungen aus den deutschen Materialprüfungsanstalten.*
N	*Nature.*
PASTM	*Proceedings of the American Society for Testing Materials.*
PIAE	*Proceedings of the Institution of Automobile Engineers.*
PIME	*Proceedings of the Institution of Mechanical Engineers.*
PRS	*Proceedings of the Royal Society*, Series A.
RM	*Revue de Métallurgie.*
RTC	*Recueil des travaux chimiques des Pays Bas et de la Belgique.*
TAIMME	*Transactions of the American Institute of Mining and Metallurgical Engineers.*
TECS	*Transactions of the Electrochemical Society.*
TFS	*Transactions of the Faraday Society.*
TIGE	*Transactions of the Institution of Gas Engineers.*
TINA	*Transactions of the Institution of Naval Architects.*
ZAC	*Zeitschrift für anorganische und allgemeine Chemie.*
ZM	*Zeitschrift für Metallkunde.*
ZPC	*Zeitschrift für physikalische Chemie, Stoichiometrie und Verwandtschaftslehre.*

LIST OF REFERENCES

arranged to serve the main purpose of an

AUTHOR INDEX

The numbers in *square brackets* represent the *pages* on which the references occur.

(*For* Abbreviations *see p.* 201)

[1] J. N. Agar quoted by U. R. Evans, *JISI* 1940, **141**, 220 P. [xxxii, 36]
[2] G. Akimow, *KM* 1932, **8**, 197. [114]
[3] A. H. W. Aten and others, *RTC* 1930, **49**, 641 ; 1931, **50**, 943. [27, 146]

[4] D. H. Bangham, *JSI* 1945, **22**, 230 ; *N* 1945, **156**, 435. [197]
[5] O. Bauer and O. Vogel, *MMPA* 1918, **36**, 114. [47]
[6] J. R. Baylis, *IEC* 1926, **18**, 370. [37]
[7] O. Beeck, " The Chemical Background for Engines Research " (Interscience Publishers). [125]
[8] G. D. Bengough, J. M. Stuart, A. R. Lee and F. Wormwell, *PRS* 1928, **121**, 88 ; 1930, **127**, 42 ; 1931, **131**, 494 ; 1931, **134**, 308 ; 1933, **140**, 399. [24, 32, 72, 74, 89, 91, 103]
[9] G. D. Bengough and L. Whitby, *JIM* 1932, **48**, 147. [151]
[10] G. D. Bengough and F. Wormwell, *ISISR* 1935, **8**, 123 ; 1936, **13**, 213. [89]
[11] G. D. Bengough and others, *JIM* 1911, **5**, 28 ; 1913, **10**, 13 ; 1916, **15**, 37 ; 1919, **21**, 167 ; 1920, **23**, 65 ; 1924, **32**, 81 ; 1928, **40**, 141. [95, 97]
[12] W. N. Bond, " Probability and Random Errors " (Arnold). [179]
[13] C. F. Bonilla, *TECS* 1945, **87**, 237. [168]
[14] C. W. Borgmann and U. R. Evans, *TECS* 1934, **65**, 249. [93]
[15] F. P. Bowden and others, *PRS* 1936, **154**, 640 ; 1939, **169**, 371, 391 ; 1939, **172**, 263 ; *N* 1942, **150**, 197. [124]
[16] S. C. Britton and U. R. Evans, *JSCI* 1930, **49**, 173 T ; 1932, **51**, 211 T ; 1936, **55**, 337 T ; 1939, **58**, 90 ; *TECS* 1933, **64**, 43. [160, 168]
[17] H. J. Bunker, *CI* 1940, p. 412. [87]

[18] W. E. Campbell and U. B. Thomas, *N* 1938, **142**, 253 ; *TECS* 1939, **76**, 303. [8
[18a] M. Centnerszwer and M. Straumanis, *ZPC* (A) 1934, **167**, 421. [59]
[19] F. A. Champion, *TFS* 1945, **41**, 593. [93]
[20] T. W. J. Chater, *JOCCA* 1941, **24**, 144. [170]
[21] G. E. Coates, *JCS* 1945, p. 484. [60]
[22] J. W. Cobb, J. W. Wood and E. Parrish, *TIGE* 1934–5, **84**, 246 ; 1935–6, **85**, 167 ; 1936–7, **86**, 58. [21]
[23] E. W. Colbeck, S. H. Smith and L. Powell, *PIME* 1943, **149**, 63, 95, 112 ; 1943, **150**, 90. [110]
[24] F. H. Constable, *PRS* 1927, **115**, 570 ; 1928, **117**, 376 ; 1929, **125**, 630. [8]
[25] R. C. Corey and T. J. Finnegan, *PASTM* 1939, **39**, 1242. [38]

[26] I. A. Denison and R. B. Darnielle, *BSJR* 1936, **17**, 363 ; 1938, **21**, 819 ; 1940, **25**, 421 ; *TECS* 1939, **76**, 199. [87]
[27] C. H. Desch, " Chemistry of Solids " (Cornelle University Press). [103]
[28] A. L. Dighton and H. A. Miley, *TECS* 1942, **81**, 321. [17]
[29] E. H. Dix, *TAIMME* 1940, **137**, 11. [114]
[30] S. F. Dorey, *TINA* 1933, **75**, 208. [124]

[31] W. N. Duff, *PIAE* 1933, **27**, 454 ; C. G. Williams, " Collected Researches on Cylinder Wear " (Institution of Automobile Engineers). [125]
[32] J. S. Dunn, *PRS* 1926, **111**, 203, 210 ; *JCS* 1929, p. 1149 ; *JIM* 1931, **46**, 25. [15, 18, 20, 194]

[33] C. A. Edwards, *JISI* 1924, **110**, 9. [111, 144]
[33a] U. R. Evans, *TFS* 1923, **19**, 201. [79]
[34] U. R. Evans, *JIM* 1923, **30**, 239 ; 1925, **33**, 27 ; *IEC* 1925, **17**, 363 ; *JCS* 1929, p. 111 ; *TECS* 1930, **57**, 407. [30, 51, 58, 93, 94]
[35] U. R. Evans, *JOCCA* 1923, **6**, 150 ; *JSCI* 1924, **43**, 315 T ; *MI* 1926, **29**, 481 ; *KM* 1930, **6**, 74. [28, 127]
[35a] U. R. Evans, *JSCI* 1924, **43**, 127 T. [96]
[36] U. R. Evans, *JCS* 1927, p. 1020 ; 1929, p. 92. [63, 108]
[37] U. R. Evans, *JIM* 1928, **40**, 99. [157, 159, 167]
[38] U. R. Evans, *JSCI* 1927, **46**, 347 T ; 1928, **47**, 55 T. [129, 130, 134]
[39] U. R. Evans, *JSCI* 1928, **47**, 62 T. [58]
[40] U. R. Evans, *TECS* 1929, **55**, 243. [158]
[41] U. R. Evans, *JCS* 1930, p. 478 ; *N* 1930, **126**, 130. [42]
[42] U. R. Evans, *TECS* 1936, **69**, 213. [135]
[43] U. R. Evans, *ISISR* 1938, **21**, 225. [6]
[44] U. R. Evans, *N* 1938, **142**, 160. [36, 147]
[45] U. R. Evans, *E* 1942, **173**, 143. [177]
[46] U. R. Evans, *TECS* Paper now in the press (1947). [194]
[47] U. R. Evans, *TFS* 1944, **40**, 120. [60]
[48] U. R. Evans, *CI* 1945, p. 106. [179]
[49] U. R. Evans, *TFS* 1945, **41**, 365. [197, 200]
[50] U. R. Evans, *MI* 1945, **67**, 114. [159]
[51] U. R. Evans and L. C. Bannister, *PRS* 1929, **125**, 370. [27]
[52] U. R. Evans and T. P. Hoar, *PRS* 1932, **137**, 343. [xxx, 34, 72]
[53] U. R. Evans and T. P. Hoar, *TFS* 1934, **30**, 424. [38]
[54] U. R. Evans and H. A. Miley, *N* 1937, **139**, 283 ; *JCS* 1937, p. 1295 ; H. A. Miley, *CSM* 1936, **25**, 197. [8]
[54a] U. R. Evans and J. Stockdale, *JCS* 1929, p. 2651. [14, 194]

[55] F. Fancutt, *JICE* 1937–8, **9**, 147. [156]
[56] G. I. Finch and A. G. Quarrell, *PRS* 1933, **141**, 398. [194]
[57] F. W. Fink, *TECS* 1939, **75**, 441. [96]
[58] G. C. Fink, W. D. Turner and G. T. Paul, *TECS* 1943, **83**, 377. [117, 124]
[59] R. A. Fisher, " Statistical Methods for Research Workers " (Oliver and Boyd). [181]
[60] H. B. Footner, *ISISR* 1938, **21**, 369. [145, 149]
[61] J. A. N. Friend and others, *JCS* 1922, **121**, 466 ; *JIM* 1925, **33**, 19. [128]
[62] K. W. Fröhlich, *ZM* 1936, **28**, 368. [20]
[63] T. C. Fry, " Probability and its Engineering Uses " (Macmillan). [176]

[64] O. Gatty and E. C. R. Spooner, " Electrode Potential Behaviour of Corroding Metals in Aqueous Solutions " (Clarendon Press). [xxx]
[65] S. Glasstone, " The Electrochemistry of Solutions " (Methuen) ; S. Glasstone, K. J. Laidler and H. Eyring, " Theory of Rate Processes ", Chapter X (McGraw-Hill) ; R. W. Gurney, " Ions in Solution " (Cambridge University Press) ; J. A. V. Butler, " Electrocapillarity " (Methuen). [xxi]
[66] R. Glauner, *KT* 1933, **3**, 36. [102]
[67] H. J. Gough, *JIM* 1932, **49**, 17 ; H. J. Gough and D. G. Sopwith, *JIM* 1932, **49**, 93 ; 1933, **52**, 57 ; 1935, **56**, 55 ; *PRS* 1932, **135**, 392. [116]
[68] A. J. Gould and U. R. Evans, *ISISR* 1939, **24**, 325. [123, 124]
[69] E. A. Gulbransen, *TECS* 1942, **81**, 327 ; 1942, **82**, 375 ; 1943, **83**, 301 ; 1945, **87**, 589 ; *IEC* (anal.) 1946, **18**, 391. [7, 12, 63]
[70] A. T. Gwathmey and A. F. Benton, *TECS* 1940, **77**, 211. [102]

71 B. P. Haigh, *JIM* 1917, **18**, 55 ; B. P. Haigh and B. Jones, *JIM* 1930, **43**, 271. [116]

72 P. Hamer, L. Powell and E. W. Colbeck, *JISI* 1945, **151**, 109 P. [138]

73 E. S. Hedges, *JCS* 1928, p. 831 ; 1930, p. 561. [62, 63]

74 E. S. Hedges, *JCS* 1925, pp. 445, 1013 ; 1926, pp. 1533, 2580, 2878 ; 1927, p. 2710 ; 1928, p. 969 ; 1929, p. 1028. [41]

75 E. S. Hedges and L. A. Jordan, *JISI* 1945, **152**, 429 P, [166]

76 E. Herzog, *BSC* 1936, **3**, 1530 ; 1938, **5**, 187. [89]

77 E. Heyn, *JIM* 1914, **12**, 3. [101]

78 T. P. Hoar, *PRS* 1933, **142**, 628. [xxxiii]

79 T. P. Hoar, *TFS* 1934, **30**, 472. [49, 92]

80 T. P. Hoar and U. R. Evans, *JCS* 1932, p. 2476. [128]

81 T. P. Hoar and D. Havenhand, *JISI* 1936, **133**, 239 P. [57, 70, 186]

82 T. P. Hoar, T. N. Morris and W. B. Adam, *JISI* 1939, **140**, 55 P ; 1941, **144**, 133 P. [166]

83 T. P. Hoar and L. E. Price, *TFS* 1938, **34**, 867. [15, 191]

84 T. P. Hoar and J. H. Schulman, *N* 1943, **152**, 102. [137]

85 C. E. Homer, *CSM* 1932, **21**, 35 ; *ISISR* 1934, **5**, 225. [137]

86 A. U. Huddle, *JISI* 1942, **146**, 262 P. [112]

87 A. U. Huddle and U. R. Evans, *JISI* 1944, **149**, 109 P. [118, 124]

88 J. C. Hudson, *TFS* 1929, **25**, 177, 475 ; *JIM* 1930, **44**, 409 ; 1935, **56**, 91. [57, 75, 81]

89 J. C. Hudson, " Protection of Iron and Steel " (Chapman & Hall). [84, 162]

90 J. C. Hudson, *ISISR* **1**, **5**, **8**, **13**, **21**. [84]

91 N. P. Inglis and G. F. Lake, *TFS* 1931, **27**, 803. [123]

92 P. A. Jacquet, *N* 1935, **135**, 1076 ; *TECS* 1936, **69**, 629, 653. [105]

93 T. H. James, *JACS* 1943, **65**, 39. [60]

94 L. Kenworthy, *JIM* 1943, **69**, 67. [48]

95 L. Kenworthy and M. D. Smith, *JIM* 1944, **70**, 463. [49, 168]

96 C. V. King, M. M. Braverman and M. Schack, *JACS* 1932, **54**, 1744 ; 1935, **57**, 1212. [59]

97 C. E. Leberknight and B. Lustman, *JOSA* 1939, **29**, 59. [8]

98 K. G. Lewis and U. R. Evans, *JSCI* 1934, **53**, 25 T. [160]

99 K. H. Logan, *TECS* 1933, **64**, 113 ; *BSJR* 1937, **19**, 695 ; 1942, **28**, 57. [88]

100 B. Lustman, *TECS* 1942, **81**, 359. [8]

101 D. J. McAdam, *PASTM* 1926, **26**, II, 224 ; 1927, **27**, II, 102 ; 1929, **29**, II, 250 ; 1930, **30**, II, 411 ; 1931, **31**, II, 259 ; 1941, **41**, 696. [116, 122]

102 D. J. McAdam and R. W. Clyne, *BSJR* 1934, **13**, 527. [122]

103 D. J. McAdam and G. W. Geil, *BSJR* 1940, **24**, 685 ; 1941, **26**, 135. [121]

104 W. Machu and O. Ungersböch, *AEHW* 1942, **15**, 301. [147]

105 J. E. O. Mayne, *JSCI* 1946, **65**, 196. [105]

106 J. E. O. Mayne and U. R. Evans, *CI* 1944, p. 109. [159]

107 R. B. Mears, *CSM* 1935, **24**, 69. [183]

108 R. B. Mears and R. H. Brown, *IEC* 1937, **29**, 1087. [187]

109 R. B. Mears and U. R. Evans, *TFS* 1934, **30**, 417. [53]

110 R. B. Mears and U. R. Evans, *TFS* 1935, **31**, 527. [24, 35]

111 J. H. G. Monypenny, " Stainless Iron and Steel " (Chapman & Hall). [65, 86]

112 H. Moore, S. Beckinsale and C. E. Mallinson, *JIM* 1920, **23**, 225 ; 1921, **25**, 35 ; 1922, **27**, 149 ; 1923, **29**, 285. [104]

113 T. N. Morris, *JSCI* 1935, **54**, 7 T. [128, 145]

114 N. F. Mott, *TFS* 1939, **35**, 1175 ; 1940, **36**, 472. [18, 194]

115 W. J. Müller and others, *TFS* 1935, **31**, 1291 ; *ZPC* 1932, **161**, 147, 411 ; 1933, **166**, 357 ; *KM* 1932, **8**, 253 ; 1935, **11**, 25 ; 1936, **12**, 132 ; 1937, **13**, 144 ; 1938, **14**, 49, 63, 77, 198. [40]

[116] L. B. Parsons, *JACS* 1925, **47,** 1830. [1]
[117] W. S. Patterson, *JSCI* 1930, **49,** 203 T. ; W. S. Patterson and L. Hebbs, *TFS* 1931, **27,** 277. [197]
[118] G. C. Peters and V. R. van Voorhis, "Statistical Procedures and their Mathematical Bases" (McGraw-Hill). [178]
[119] L. B. Pfeil, *JISI* 1929, **119,** 501 ; 1931, **123,** 237. [14, 15, 191]
[120] N. B. Pilling and R. E. Bedworth, *JIM* 1923, **29,** 529. [7, 11, 12, 13, 15]
[121] A. M. Portevin, E. Prétet and H. Jolivet, *RM* 1934, **31,** 101, 130, 219 ; *JISI* 1934, **130,** 219. [20, 194]
[122] L. E. Price, *CI* 1937, p. 769. [193]
[123] L. E. Price and G. J. Thomas, *JIM* 1938, **63,** 21, 29 ; 1939, **65,** 247. [20, 23, 191, 193]
[124] L. E. Price and G. J. Thomas, *TECS* 1939, **76,** 329. [10, 23]

[125] W. D. Richardson, *TECS* 1920, **38,** 265. [57]
[126] B. E. Roetheli and G. L. Cox, *IEC* 1931, **23,** 1084. [137]
[127] E. C. Rollason, *JIM* 1937, **60,** 35. [153]
[128] W. Rosenhain and later investigators of the National Physical Laboratory, *JISI* 1931, **123,** 259 ; 1934, **130,** 279 ; 1941, **143,** 136 P. [112]

[129] G. Schikorr, *MMPA* 1933, Sonderheft 22. [93]
[130] R. Seligman and P. Williams, *JSCI* 1916, **35,** 88 ; 1918, **37,** 159 T. [66]
[131] M. Smialowski, *KM* 1938, **14,** 111. [109]
[132] H. Sutton and L. F. le Brocq, *JIM* 1935, **57,** 199. [150]
[133] H. Sutton and A. J. Sidery, *JIM* 1927, **38,** 241. [150]
[134] Symposium, *IEC* 1945, **37,** 703–59 and 842–6. [127]
[135] Symposium on Stress-Corrosion Cracking (American Society for Testing Materials and American Institute of Mining and Metallurgical Engineers) 1944 [104, 105]

[136] G. Tammann, *ZAC* 1919, **107,** 1. [176]
[137] G. Tammann and W. Boehme, *ZAC* 1934, **217,** 225. [12]
[138] G. Tammann and others, *ZAC* 1920, **111,** 78 ; 1922, **123,** 196 ; 1922, **124,** 25 ; 1923, **128,** 179 ; 1925, **148,** 297. [8]
[139] A. A. Taylor and J. W. Cobb, *TIGE* 1938–9, 88, 106. [22]
[140] M. Tchorabdji-Simnad and U. R. Evans, *PRS.* 1947, **188,** 372 [119]
[141] M. de Kay Thompson, *TECS* 1940, **78,** 251. [38]
[142] R. S. Thornhill, *JISI* 1942, **146,** 73 P ; *IEC* 1945, **37,** 706. [79, 135]
[143] R. S. Thornhill and U. R. Evans, *JCS* 1938, pp. 614, 2109. [32, 36]
[144] L. Tronstad and others, *TFS* 1933, **29,** 502 ; 1934, **30,** 349, 362 ; 1935, **31,** 1151. [8, 63]
[145] T. H. Turner, *PIME* 1943, **149,** 77. [141]

[146] C. van Brunt and E. J. Remscheid, *GER* 1936, **39,** 128. [139]
[147] W. H. J. Vernon, *TFS* 1923, **19,** 839 ; 1927, **23,** 113. [7, 12, 13, 23, 74, 85, 197]
[148] W. H. J. Vernon, *JCS* 1926, p. 2273. [194]
[149] W. H. J. Vernon, *TFS* 1931, **27,** 255, 582. [80]
[150] W. H. J. Vernon, *JIM* 1932, **48,** 121. [74]
[151] W. H. J. Vernon, *TFS* 1935, **31,** 1668. [1, 85]
[152] W. H. J. Vernon, *JISI* 1940, **142,** 183 P. [76]
[153] W. H. J. Vernon, E. I. Akeroyd and E. G. Stroud, *JIM* 1939, **65,** 301. [11, 17]
[154] W. H. J. Vernon and E. G. Stroud, *N* 1938, **142,** 477, 1161. [105]
[155] W. H. J. Vernon and L. Whitby, *JIM* 1929, **42,** 181 ; 1930, **44,** 389 ; 1932, **49,** 153. [81]
[156] W. H. J. Vernon, F. Wormwell and T. J. Nurse, *JCS* 1939, p. 621 ; *JISI* 1944, **150,** 81 P. [7, 10]
[157] A. von Zeerleder, *JIM* 1931, **46,** 177 ; 1941, **67,** 87. [114]

[158] R. Vondráček and J. Izák-Krizko, *RTC* 1925, **44**, 376. [59]
[159] J. T. Waber, H. J. McDonald and B. Longtin, *TECS* 1945, **87**, 209. [110]
[160] C. Wagner and others, *ZPC* (B) 1933, **22**, 199, 212 ; 1934, **25**, 71, 209 ; 1938, **40**, 455. [15, 191, 197]
[161] J. H. Whiteley and A. F. Hallimond, *CSM* 1918, **9**, 1 ; 1925, **14**, 163. [103]
[162] W. G. Whitman and R. P. Russell, *IEC* 1924, **16**, 276. [47]
[163] N. T. M. Wilsmore, *ZPC* 1900, **35**, 291. [xxiv]
[164] A. B. Winterbottom, *N* 1937, **140**, 364 ; *TFS* 1946, **42**, 487. [8]

[165] G. U. Yule and M. G. Kendall, " Introduction to the Theory of Statistics " (Griffin). [181]

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